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PROTEIDS OF THE HORSE BEAN (*Vicia faba*).[1]

BY THOMAS B. OSBORNE AND GEORGE F. CAMPBELL.

Received March 29, 1898.

THE only references which we have found to investigations of the proteids of this seed that at present have any importance are contained in papers by Ritthausen.[2]

In his earlier work[3] Ritthausen described as legumin the proteid extracted from the horse bean by potash water. Later[4], he gave the results of treating the earlier preparations with salt solution and also of extracting the seeds with brine and precipitating the dissolved proteid by dilution or by acids, and concluded that the preparations which he obtained were mixtures of two proteids which could only be separated by dissolving in acid or alkali, precipitating by neutralization and extracting the precipitate with brine; the part dissolving he regarded as conglutin; that undissolved as legumin. A careful study of Ritthausen's work leaves us in much doubt respecting the nature of the proteids of this seed, and we have therefore undertaken the present investigation.

In order to avoid contaminating our preparations with tannin, which Ritthausen found to be present in considerable quan-

[1] Reprinted from advance sheets of the Report of the Connecticut Agricultural Experiment Station for 1897. Communicated by the authors.

[2] Early references to legumin have been already noticed in our paper on "Legumin of the Pea and Vetch," Report of this Station for 1895, p. 262. This Journal, 18, 583.

[3] Die Eiweisskorper, etc., Bonn, 1872, p. 170.

[4] *J. prakt. Chem.*, 26, 504, and 29, 448.

tity in the skin of these beans, we removed the greater part of the outer coating from the coarsely broken seeds by a current of air and the remainder by hand-picking. In this way it was possible to separate the brown outer seed-coat completely and by then grinding the broken beans to obtain a flour free from tannin.

A preliminary extraction made with this flour gave us a large yield of proteid which, in general, had nearly the properties and composition of the products similarly obtained from the pea and lentil, but differed throughout in containing less carbon than the corresponding substances from these other seeds, and in being, to a considerable extent, soluble in water. As these aqueous solutions reacted strongly acid with litmus and when neutralized gave precipitates soluble in brine which were reprecipitated by dilution, we were led to believe that the differences which we had found between the proteids of this seed and those of the pea, lentil, and vetch were due to a combination of the proteids with the acid of the seed. As this view appeared to be confirmed, we omit further details of our first extraction and proceed to an account of the second.

Two kilograms of the bean flour were treated with ten liters of ten per cent. salt solution, protected with thymol, and left over night in a cool place. The extract was strained through fine bolting-cloth and allowed to deposit suspended matter during two hours. The turbid liquid was siphoned off, centrifugated, and filtered nearly clear. The extract was then saturated with ammonium sulphate, the precipitate produced filtered out, removed from the paper, suspended in a little water and dialyzed for twenty-four hours, whereby so much of the sulphate was removed that the proteid dissolved. The solution so obtained was then filtered perfectly clear through a pulp filter and dialyzed for forty-four hours. The precipitate which had formed at first separated in spheroids, but these on settling united to a coherent mass, A, from which the solution B was decanted.

A portion of the precipitate A, weighing twenty-eight grams when air-dry, was washed thoroughly with water (in which it partly dissolved) and then with alcohol and dried at 110° for analysis.

LEGUMIN, 76.[1]

Carbon	51.55
Hydrogen	6.91
Nitrogen	18.12
Sulphur	0.48
Oxygen	22.94
	100.00
Ash	0.54

The remainder of precipitate A was dissolved in brine and the resulting solution, having an acid reaction, was neutralized to litmus by adding very dilute potash water. This required 0.36 gram of potassium hydroxide. The slightly turbid solution was filtered absolutely clear and dialyzed for forty-eight hours. The large precipitate which resulted was found to dissolve completely in brine and to yield a perfectly neutral solution, which, when heated in a boiling water-bath, gave some coagulum. A portion of this precipitate was washed with water and alcohol, dried at 110°, and analyzed.

LEGUMIN, 77.

Carbon	51.87
Hydrogen	6.97
Nitrogen	18.05
Sulphur	0.38
Oxygen	22.73
	100.00
Ash	0.84

The remainder of this substance was dissolved in 250 cc. of three per cent. brine and the solution diluted to 600 cc. A rapidly settling precipitate resulted which formed a fluid deposit from which the somewhat turbid mother-liquor was soon decanted; the proteid was washed thoroughly with water and alcohol, yielding when dry 19.13 grams of preparation 78.

LEGUMIN, 78.

Carbon	51.79
Hydrogen	7.06
Nitrogen	18.10
Sulphur	0.40
Oxygen	22.65
	100.00
Ash	0.79

[1] Numbered consecutively with the preparations of the proteids of the lentil. This Journal, 20, 362.

The solution decanted from 78 was diluted with 150 cc. of water and a second precipitate obtained, wholly like the first, which when dried weighed eleven grams and had the following composition :

LEGUMIN, 79.

Carbon	51.90
Hydrogen	6.94
Nitrogen	18.12
Sulphur	0.38
Oxygen	22.66
	100.00
Ash	0.59

The solution from which 79 had separated was further diluted with 500 cc. of water and allowed to stand over night in a cool room. The next morning the solution was decanted from a small precipitate that had settled out. This, after drying, weighed five grams and had the following composition :

LEGUMIN, 80.

Carbon	51.92
Hydrogen	7.04
Nitrogen	18.11
Sulphur	0.30
Oxygen	22.63
	100.00
Ash	0.60

The solution decanted from 80 was dialyzed for four days but only a trace of proteid separated. Preparations 78, 79, and 80 contained no trace of coagulable proteid and may therefore be considered to be pure legumin. Since, however, 77, of which these were fractions, was shown by this treatment to contain only a very little coagulable matter, it too is essentially pure legumin as indicated by the analysis.

Solution B, described on page 394, was further dialyzed for twenty-four hours and the resulting precipitate C filtered out and the filtrate D treated as described on page 397.

The precipitate C was dissolved in ten per cent. brine, and the resulting solution diluted until it contained one per cent. of salt. The precipitate that formed was filtered out and the filtrate added to solution D. The precipitate was again dissolved in

salt solution, filtered clear, exactly neutralized with dilute potash water, and dialyzed for forty-eight hours.

The globulin which had separated was filtered out. The filtrate contained a little more proteid, which yielded a coagulum on heating in a boiling water-bath.

The globulin was dissolved in 200 cc. of two per cent. brine, and the solution diluted with 200 cc. of water, which threw down a precipitate from which the solution E was decanted and treated as further described, while the precipitate was redissolved in salt solution, which was then dialyzed for twenty-four hours.

The precipitate which finally resulted, after washing and drying, weighed sixteen grams, and when dried at 110° had the following composition:

GLOBULIN, 81.

Carbon	51.89
Hydrogen	7.03
Nitrogen	17.67
Sulphur	0.34
Oxygen	23.07
	100.00
Ash	0.76

The solution filtered from 81 contained but little proteid, which coagulated on heating to 99°.

Solution E, on diluting with an equal volume of water, gave a precipitate that, when washed and dried, weighed 4.74 grams, having the following composition:

GLOBULIN, 82.

Carbon	52.31
Hydrogen	7.04
Nitrogen	17.70
Sulphur	0.21
Oxygen	22.74
	100.00
Ash	0.57

Solution D, noted on page 396, being inconveniently bulky, was saturated with ammonium sulphate, and the precipitate thus separated was dissolved in a little water; the solution was filtered clear, and dialyzed for five days. The deposited substance was

filtered out and the filtrate F treated as described later. The precipitate was dissolved in brine, the solution obtained was filtered clear and dialyzed for three days whereby all but a trace of the proteid was precipitated. This was filtered out, dissolved in 100 cc. of two per cent. salt solution and precipitated by adding fifty cc. of water. After the proteid, thus thrown down, had settled, the supernatant liquid was decanted and fifty cc. more water added, which caused a second precipitation. The solution from which this had separated was then dialyzed and the globulin contained in it precipitated. Thus three successive fractions were obtained which, when washed and dried, weighed respectively 5.65, 3.87, and 2.73 grams. When dried at 110° and analyzed these were found to have the following composition:

VICILIN.

	83	84	85
Carbon	52.53	52.53	52.40
Hydrogen	6.93	6.98	7.09
Nitrogen	17.18	17.61	17.54
Sulphur	0.19	0.10	0.13
Oxygen	23.07	22.78	22.84
	100.00	100.00	100.00
Ash	0.26	0.18	0.13

Filtrate F, from which the substance yielding the three preceding preparations had been derived, was further dialyzed for seven days until freed from sulphates, which caused the separation of a small precipitate that, when filtered out, washed, and dried, weighed 1.64 grams and gave the following results on analysis:

PROTEID, 86.

Carbon	52.43
Hydrogen	6.87
Nitrogen	16.42
Sulphur, Oxygen	24.28
	100.00
Ash	0.28

The filtrate from 86 was then heated to just 60° for about two hours, which caused a coagulum that was filtered out, washed

with hot water and with alcohol, dried, and found to weigh 1.60 grams. The filtrate from this coagulum was heated for some time at 75° and a second coagulum obtained, weighing 1.80 grams. Dried at 110°, the two preparations had the following composition:

LEGUMELIN.

	87	88
Carbon	52.81	52.98
Hydrogen	6.98	6.89
Nitrogen	16.49	16.43
Sulphur	23.72	1.32
Oxygen		22.38
	100.00	100.00
Ash	0.23	0.33

These two preparations are probably legumelin, although their carbon is distinctly less than that found in our preparations from other leguminous seeds. Since the solution from which these preparations separated had not been previously neutralized, we are inclined to ascribe this difference to an acid combined with the proteid.

The filtrate from 88 was next dialyzed against alcohol until all proteid matter was precipitated. This was filtered out, washed with absolute alcohol, dried, and found to weigh 6.78 grams. This preparation was dissolved in a little water, filtered from a slight insoluble residue; the solution was dialyzed for five days, then heated to boiling, and filtered from a trace of coagulum. The filtrate, which gave no precipitate on saturating with salt, was then concentrated to small volume over a water-bath and precipitated by pouring into alcohol. In this way 4.45 grams of proteose was obtained, which, when dried at 110° and analyzed, was found to have the following composition:

PROTEOSE, 89.

Carbon	50.24
Hydrogen	6.66
Nitrogen	17.11
Sulphur	1.87
Oxygen	24.12
	100.00
Ash	0.48

In order to confirm the foregoing results another extraction was made by treating 1200 grams of bean meal with 4200 cc. of water containing 9.44 grams of baryta, just enough to saturate the acid of the seed, using litmus as an indicator. This amount was ascertained by a careful preliminary test with 100 grams of the meal using a carefully standardized solution of baryta. After thoroughly mixing the meal with the water, an equal volume of ten per cent. brine was added, causing the gummy meal residue to separate in masses which settled quite rapidly and left the solution comparatively clear.

The residue was then strained out on fine bolting-cloth and the extract allowed to stand a short time, when it was siphoned from the sediment, filtered nearly clear, and saturated with ammonium sulphate. The precipitate produced was filtered out, suspended in water, and dialyzed over night. The next morning the solution of the proteid, which had resulted on dialyzing away the greater part of the adherent sulphate, was filtered and dialyzed for four days. A large precipitate of globulin separated which was filtered out and the filtrate G was treated as is subsequently described. The precipitate was redissolved in brine, filtered perfectly clear, and dialyzed for forty-two hours, whereby a large amount of globulin separated in form of spheroids that united on settling to a coherent mass. From this the solution H was decanted almost completely. The precipitate was dissolved in 500 cc. of two per cent. salt solution and the globulin again thrown down by diluting the salt solution to 1.33 per cent. After the large precipitate produced had settled, the solution I was decanted and the globulin redissolved in 100 cc. of ten per cent. brine and precipitated by diluting to 750 cc. As the substance still contained some coagulable matter it was redissolved four times in fifty cc. of ten per cent. brine and precipitated by diluting to 500 cc. The final precipitate gave only an opalescence on heating its solution in a boiling water-bath. Washed with water and with alcohol and dried over sulphuric acid, this preparation weighed forty-one grams, and had the following composition when dried at 110°:

LEGUMIN, 90.

Carbon	51.55
Hydrogen	7.03
Nitrogen	17.95
Sulphur	0.38
Oxygen	23.09
	100.00
Ash	0.15

Solutions G, H, I, and those from the four last precipitations of 90 were separately dialyzed and the globulin which deposited was all dissolved together by adding fifty cc. of ten per cent. brine to water in which the substance was suspended. The resulting solution contained one and seven-tenths per cent. of salt and was diluted to a content of one and three-tenths per cent. This gave a precipitate on which the same treatment was repeated. The two solutions decanted from these precipitations were united and diluted with 200 cc. of water, the precipitate was united with the twice precipitated proteid just described and the solution J set aside for further treatment. The united precipitates were dissolved with fifty cc. of ten per cent. salt solution, and water added to 400 cc. The precipitate produced, which still yielded some opalescence in the boiling water-bath, was washed with water and alcohol, and, when dried, weighed 15.93 grams, and had the following composition :

LEGUMIN, 91.

Carbon	51.72
Hydrogen	6.95
Nitrogen	18.00
Sulphur	0.42
Oxygen	22.91
	100.00
Ash	0.18

The solution decanted from 91 was united with solution J, before noticed, and diluted until the salt content was one per cent. After standing over night, the solution was decanted from the precipitate, which when washed and dried over sulphuric acid weighed nine and eight-tenths grams, and when dried at 110° had the following composition :

LEGUMIN, 92.

Carbon	51.70
Hydrogen	7.12
Nitrogen	18.05
Sulphur	0.36
Oxygen	22.77
	100.00
Ash	0.16

The solution decanted from 92 was dialyzed free from chlorides, the precipitate produced dissolved in one per cent. brine, and the solution diluted with an equal volume of water. After the proteid which separated had settled out, the solution was decanted and the deposit was washed with water and alcohol. When dry 14.41 grams of proteid were obtained, which were analyzed with the following results:

GLOBULIN, 93.

Carbon	52.14
Hydrogen	7.08
Nitrogen	17.59
Sulphur	0.15
Oxygen	23.04
	100.00
Ash	0.13

By adding a quantity of water to the solution decanted from 93 the globulin remaining in solution was precipitated and gave, when dried, 5.80 grams of proteid of the following composition:

VICILIN, 94.

Carbon	52.36
Hydrogen	7.12
Nitrogen	17.43
Sulphur	0.10
Oxygen	22.99
	100.00
Ash	0.10

Solution G, page 400, was saturated with ammonium sulphate, and the proteid thereby precipitated was dissolved in water, the solution filtered perfectly clear and dialyzed six days, when the precipitate produced was filtered out, washed, and treated as usual, giving preparation 95, weighing 4.23 grams.

PROTEID, 95.

Carbon	52.21
Hydrogen	7.12
Nitrogen	16.50
Sulphur	1.23
Oxygen	22.94
	100.00
Ash	0.33

The filtrate from 95 was then heated to 65° in a water-bath, the coagulum filtered out, and the filtrate heated to 85°, which caused a second coagulum. The two preparations, 96 and 97, were washed with hot water, dehydrated with absolute alcohol, dried, and found to weigh 3.47 grams and 1.38 grams, respectively.

LEGUMELIN.

	96	97
Carbon	52.68	53.29
Hydrogen	7.14	7.05
Nitrogen	15.96	16.00
Sulphur	1.33	1.24
Oxygen	22.89	22.42
	100.00	100.00
Ash	0.25	0.31

The filtrate from 97 gave no coagulum on boiling and was therefore saturated with salt, but as no precipitate formed, salt saturated acetic acid was added as long as proteid was thereby separated. The resulting precipitate was dissolved in water, filtered clear, and dialyzed till free from chlorides. The salt saturated filtrate was neutralized with sodium carbonate and also dialyzed till free from chlorides. Both solutions were next dialyzed in alcohol until concentrated to small volume, then were treated with excess of alcohol, and the precipitates obtained were filtered out. That from the salt saturated solution amounted to hardly more than a trace, while that from the acetic acid precipitate 98 weighed 4.14 grams.

PROTOPROTEOSE, 98.

Carbon	49.96
Hydrogen	6.76
Nitrogen	16.95
Sulphur	2.75
Oxygen	23.58
	100.00
Ash	0.28

The large amount of sulphur found in this preparation was confirmed by a second closely agreeing determination. The small quantity of ash and the method of preparation make it impossible that this sulphur could be due to admixture of either calcium sulphate or ammonium sulphate.

In the horse bean, as in the pea and lentil, the proteids soluble in salt solution are legumin, vicilin, legumelin, and proteose. In the following tables the analyses of the purer preparations of these proteids may be readily compared:

LEGUMIN.

	76	77	78	79	80	90	91	92	Aver.
Carbon	51.55	51.87	51.79	51.90	51.92	51.55	51.47	51.70	51.72
Hydrogen	6.91	6.97	7.06	6.94	7.04	7.03	7.02	7.12	7.01
Nitrogen	18.12	18.05	18.10	18.12	18.11	17.95	18.00	18.05	18.06
Sulphur	0.48	0.38	0.40	0.38	0.30	0.38	0.42	0.36	0.39
Oxygen	22.94	22.73	22.65	22.66	22.63	23.09	23.09	22.77	22.82
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

VICILIN.

	82	83	84	85	93	94	Aver.
Carbon	52.31	52.53	52.53	52.40	52.14	52.36	52.38
Hydrogen	7.04	6.93	6.98	7.09	7.08	7.12	7.04
Nitrogen	17.70	17.28	17.61	17.54	17.59	17.43	17.52
Sulphur	0.21	0.19	0.10	0.13	0.15	0.13	0.15
Oxygen	22.74	23.07	22.78	22.84	23.04	22.99	22.91
	100.00	100.00	100.00	100.00	100.00	100.00	100.00

LEGUMELIN.

	87	88	96	97	Aver.
Carbon	52.81	52.98	52.68	53.29	52.94
Hydrogen	6.98	6.98	7.14	7.05	7.02
Nitrogen	16.49	16.43	15.96	16.00	16.22
Sulphur	23.72	1.32	1.33	1.24	1.30
Oxygen		22.38	22.89	22.42	22.52
	100.00	100.00	100.00	100.00	100.00

PROTEOSE.

	89	98
Carbon	50.24	49.95
Hydrogen	6.66	6.76
Nitrogen	17.11	16.95
Sulphur	1.87	2.75
Oxygen	24.12	23.58
	100.00	100.00

In order to determine the amount of the proteids of this seed extracted by water, 200 grams of the fine meal were thoroughly mixed with 2000 cc. of water so that all lumps were broken up, and the coarse residue was strained out on bolting-cloth. After standing two hours, the greater part of the starch, etc., settled, and 1400 cc. of extract were siphoned off and filtered perfectly clear on a pulp filter, the first 300 cc. being rejected and the next 1000 cc. collected separately. The latter was dialyzed for four days, in which time all the proteid separable in this way deposited as spheroids. The precipitate, washed and dried, was equal to sixteen per cent. of the meal.

The process just described was exactly repeated save that enough baryta was at first added to make the extract neutral to litmus: the yield of proteid was eighteen per cent.

The proteid from the first extraction contained 1.16 per cent. of ash and, reckoned ash-free, 17.50 per cent. of nitrogen, showing it to be nearly pure globulin, while that from the second, neutralized extract, was less pure, as it contained 5.41 per cent. of ash and contained, ash-free, 16.96 per cent. of nitrogen. The reactions of these extracts were compared under identical conditions with the following result:

Both extracts, like those from the pea, lentil, and vetch, when poured into water gave, where the two fluids came in contact, a slight cloud which disappeared on shaking. Unlike the neutralized extract, as well as unlike both neutral and acid extracts of the other legumes, the unneutralized extract of the horse bean gave a heavy precipitate with sodium chloride, even with perfectly pure salt which we prepared from *pure* soda and *pure* hydrochloric acid and proved to be absolutely neutral. This precipitation of the globulin would indicate the presence of an acid compound, but the extract gave but a very slight precipitate on neutralizing with baryta, probably due to phosphates. The addition of acetic acid gave a large precipitate soluble in dilute brine, as did calcium chloride and calcium sulphate.

PROTEIDS OF THE VETCH.[1]

By Thomas B. Osborne and George F. Campbell.

Received March 29, 1898.

In order to further fractionate vetch globulin, we treated a quantity of preparation 17[2] with 900 cc. of three per cent. brine and, after filtering out the insoluble residue, we added an equal volume of water to the clear filtrate, and then cooled the mixture to 5°. The precipitate thus caused was washed and dried, forming preparation 99,[3] and the filtrate was diluted with an equal volume of water, which caused a second precipitate, preparation 100. The residue, insoluble in the three per cent. brine, had become swollen and gelatinous, as has always been observed with the insoluble form of legumin, so that it stopped the pores of the filter. It was therefore washed by decantation with salt solution and finally with water. As the salt was washed out the substance lost its gelatinous properties and became granular and easily filtered. It was next treated with one per cent. sodium carbonate solution, and the small portion insoluble therein was filtered out. The solution was partly neutralized with hydrochloric acid, and carbonic acid gas passed through it, which precipitated nearly all the dissolved proteid. This was filtered out, dissolved in brine, and the clear solution dialyzed. The substance thus separated, when washed and dried, formed preparation 101.

These three preparations were carefully analyzed with the following results:

Legumin.

	99	100	101
Carbon	51.72	51.52	51.79
Hydrogen	6.97	6.95	7.03
Nitrogen	18.13	18.08	18.03
Sulphur	0.43	23.47	23.15
Oxygen	22.75		
	100.00	100.00	100.00

[1] Reprinted from advance sheets of the Report of the Connecticut Agricultural Experiment Station for 1897. Communicated by the authors.

[2] Annual Report of the Connecticut Agricultural Experiment Station for 1895, p. 277. This Journal, 18, 598.

[3] Numbered consecutively with the preparations of the proteids of the horse bean.

Another extraction was made by treating 500 grams of vetch meal with water and then with ten per cent. sodium chloride solution. After filtering clear, the salt extract was saturated with ammonium sulphate, the precipitate produced was dissolved in brine, the solution filtered perfectly clear, and dialyzed. In this way thirty-five grams or seven per cent. of the meal was obtained as preparation 102, having the following composition:

LEGUMIN, 102.

Carbon	51.62
Hydrogen	6.92
Nitrogen	17.88
Sulphur	0.50
Oxygen	23.08
	100.00
Ash	0.23

Again, a quantity of vetch meal was digested in saturated salt solution and the dissolved legumin precipitated by dialysis. After drying at 110° this gave the following figures:

LEGUMIN, 103.

Carbon	51.86
Hydrogen	6.99
Nitrogen	17.97
Sulphur, Oxygen	23.18
	100.00
Ash	0.57

Another extraction was made by treating 1200 grams of meal with three liters of water containing enough baryta to exactly neutralize the acid of the seed when tested with litmus paper. After thoroughly mixing, three liters of ten per cent. salt solution were added and the residual meal strained out on fine bolting-cloth. After standing a short time the greater part of the starch settled and the liquid was siphoned off, filtered perfectly clear, and saturated with ammonium sulphate. The precipitate produced was filtered out, suspended in water, and dialyzed over night, whereupon the proteid dissolved. Its solution was filtered clear and dialyzed for two days with separation of a large precipitate.

This was filtered out and the filtrate A examined as will be described later. The precipitate was dissolved in brine, the solution filtered perfectly clear from a small amount of insoluble matter, and dialyzed for two days. The large coherent deposit was washed with water and with alcohol, and dried over sulphuric acid. This preparation, 104, weighed seventy-five grams and, as it was obtained from nearly three-fourths of the total extract, represented about ten per cent. of the meal. When dried at 110° and analyzed, the following results were obtained:

LEGUMIN, 104.

Carbon	51.59
Hydrogen	7.07
Nitrogen	18.03
Sulphur	0.36
Oxygen	22.95
	100.00
Ash	0.15

The filtrate A was returned to the dialyzer and, after three days, filtered from a small precipitate which, washed and dried, weighed six and a half grams and gave preparation 105, having the following composition:

PROTEID, 105.

Carbon	51.81
Hydrogen	7.10
Nitrogen	17.07
Sulphur	0.57
Oxygen	23.45
	100.00
Ash	0.38

The filtrate from 105 was saturated with ammonium sulphate and the precipitate produced filtered out, dissolved in as small a quantity of water as possible, the solution filtered clear, and dialyzed for seven days, when it was filtered from a small precipitate that was partly soluble in salt solution. This was washed with water and alcohol and formed preparation 106.

The filtrate from 106 was heated to 65° in a large water-bath and a coagulum obtained which, when filtered out, washed, and dried, formed preparation 107, weighing three and two-tenths grams. The filtrate from this, on heating to 85°, gave a small

coagulum that, when washed and dried, weighed only 0.88 gram, 108.

LEGUMELIN.

	106	107	108
Carbon	53.05	53.33	....
Hydrogen	7.29	6.93	....
Nitrogen	16.25	16.10	16.16
Sulphur	1.19	0.85	....
Oxygen	22.22	22.79	....
	100.00	100.00	....
Ash	0.39	0.26	0.38

The filtrate from 108 gave no coagulum on boiling. It was concentrated, partially by evaporation and further by dialysis in alcohol. A small precipitate thus separated, which was dehydrated with absolute alcohol and dried, giving one gram of preparation 109, that contained 12.74 per cent. of ash and, reckoned ash-free, 15.71 per cent. of nitrogen.

The results show that the salt extracts of the vetch seed contain no other proteids than legumin, legumelin, and a very small proportion of proteose. Vicilin, which was found in the pea, horse bean, and lentil, is not present in detectable quantity in the vetch.

Our new analyses of these proteids are tabulated as follows:

LEGUMIN.

	99	100	101	102	103	104	Aver.	Former Aver.
Carbon	51.72	51.52	51.79	51.62	51.86	51.59	51.69	52.09
Hydrogen	6.97	6.95	7.03	6.92	6.99	7.07	6.99	6.88
Nitrogen	18.13	18.08	18.03	17.88	17.97	18.03	18.02	18.02
Sulphur	0.43	23.45	23.15	0.50	23.18	0.36	0.43	0.46
Oxygen	22.75			23.08		22.95	22.87	22.55
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

LEGUMELIN.

	20	106	107	108	Aver.
Carbon	53.55	53.05	53.33	....	53.31
Hydrogen	6.70	7.29	6.93	....	6.97
Nitrogen	16.46	16.25	16.10	16.16	16.24
Sulphur	1.02	1.19	....	....	1.11
Oxygen	22.27	22.22	....	....	22.37
	100.00	100.00	....	....	100.00

PROTEOSE, 22.

Carbon	50.85
Hydrogen	6.75
Nitrogen	16.65
Sulphur, Oxygen	25.75
	100.00

THE PROTEIDS OF THE PEA, LENTIL, HORSE BEAN, AND VETCH.[1]

BY THOMAS B. OSBORNE AND GEORGE F. CAMPBELL.

Received March 29, 1898.

As shown in our papers on the proteids of the pea, lentil, horse bean, and vetch, these seeds contain legumin, legumelin, and proteose, and the three first-named also contain vicilin. A careful comparison of the reactions and properties of these proteids, as now obtained by us, reveals no difference between preparations of the same substance from different seeds.

LEGUMIN.

Legumin forms the chief proteid constituent obtainable from the vetch, pea, lentil, and horse bean. In the first-named seed about ten per cent. of the meal was found to consist of legumin; in the three other seeds this proteid is associated with vicilin, from which we have no method for its quantitative separation. From the pea about ten per cent., from the lentil thirteen per cent., and from the horse bean about seventeen per cent. of these mixed proteids were obtained. The lentil contains the least proportion of legumin, which seems to form about two-thirds of the mixed proteids, while the horse bean contains the greatest, as in this seed vicilin is present in relatively small amount.

Legumin is a globulin, for it dissolves readily in saline solutions and is precipitated therefrom either by dialysis, dilution, or cooling. By dialysis or by cooling it separates in the form of spheroids which, after settling from the solution, unite to form a plastic mass. By diluting its concentrated solutions the legumin separates as a viscid, translucent fluid. This fluid, when

[1] Reprinted from advance sheets of the Report of the Connecticut Agricultural Experiment Station for 1897. Communicated by the authors.

treated with water, becomes opaque and solid, so that the legumin can be converted into a coarse meal by rubbing with a glass rod under water. Conglutin from lupin seeds and amandin from almonds behave similarly, as do gliadin of wheat and rye and hordein of barley, when precipitated from alcoholic solutions by dilution with water.

Solutions containing more than two per cent. of sodium chloride dissolve legumin abundantly; those containing less salt have a solvent power rapidly decreasing with the diminishing salt content so that a one per cent. salt solution dissolves very little. Saturation with sodium chloride or magnesium sulphate does not precipitate legumin from its solution in brine, but saturation with sodium sulphate at 34° precipitates it almost completely.

In pure water legumin is entirely insoluble, but if the solution from which the legumin is precipitated contains acid, this may combine with the legumin and the resulting preparation, like other acid globulins, will then dissolve in pure water.

If seeds containing legumin are extracted with water, more or less of the legumin is dissolved; from the pea about four per cent., from the vetch two and a half per cent., from the lentil ten per cent., and from the horse bean sixteen per cent. The legumin thus dissolved is largely precipitated by dialysis in water, by the addition of acids and by lime salts and very slightly by great dilution with water. These aqueous extracts react strongly acid with litmus, and alkaline with lacmoid, a behavior doubtless due to acid potassium phosphates together with organic acids or acid salts, for acids combined with proteids do not react with lacmoid, although they readily turn blue litmus red. Solutions which we have made, of legumin from various seeds as well as of edestin from hemp-seed, by dissolving the proteid in monohydrogen potassium phosphate, have shown us all the reactions of these aqueous extracts excepting one presented by the horse bean, the unneutralized water extracts of which are precipitated with *pure* sodium chloride. This reaction we cannot explain, for these extracts give with dilute acids precipitates soluble in salt solutions and no precipitates on neutralization, reactions which seem to exclude the presence of acid globulin.

Solutions of legumin or of edestin in monohydrogen potassium phosphate behave more like solutions in dilute alkali carbonates than like solutions in neutral salts, for they give precipitates with dilute acids which are soluble in more acid or in salt solutions and are not precipitated by dilution unless very little phosphate is present. If phosphoric acid is added to the potassium phosphate solution, the solvent power of the phosphate is diminished and the facility with which the proteid is precipitated by dilution is increased; but if only little acid is added, yet enough to give a decided reaction with litmus, considerable quantities of the globulins are still dissolved and the reactions of solutions so made closely resemble those of the aqueous extracts of these seeds. As a result of numerous comparisons of the reactions of solutions so prepared with those of the aqueous extracts of leguminous seeds, we believe that the extraction of legumin by water from these seeds is due to the presence of acid potassium salts of phosphoric and organic acids, and that in consequence of the varying proportions of these substances in the different kinds of seeds, different amounts of legumin are thus extracted from them. As the proportion of phosphoric acid to potash in these leguminous seeds is much smaller than in most of the other seeds which we have examined, the character of the salts present may fairly be supposed to differ, and consequently the solubility of the proteids would also differ when the seeds are extracted with water. Thus in lupin seeds the amount of phosphoric acid, one and four-tenths per cent., exceeds that of the potash, one and one-tenth per cent., and from them water extracts but little proteid. Liebig and Ritthausen attributed the solubility of legumin to *basic* phosphates, and the latter undertook extensive experiments to show the presence of an excess of potash in the aqueous extracts, but such a supposition appears to overlook the fact that the aqueous extracts of these seeds are decidedly acid towards litmus.

Dissolved in dilute sodium chloride solution, legumin is precipitated by a little acetic acid, the precipitate being soluble in an excess of sodium chloride. The solubility of precipitates so produced depends on the relative proportions of salt and acid.

Legumin extracted without neutralizing the natural acid of the seed and precipitated by dialysis, either directly or after pre-

cipitation with ammonium sulphate, is usually converted to a large extent into insoluble "albuminate."

This "albuminate" differs from the similar insoluble products obtained from most other globulins, for when treated with salt solution it becomes gelatinous, cannot be filtered, and, on washing with water, shrinks, becomes opaque, and finally granular, so that it can be very readily washed on a filter. This substance appears to become hydrated by salt solution and dehydrated by pure water.

If the acid of the seed is previously neutralized, the globulin extracted by salt solution yields very little if any insoluble "albuminate," which indicates that the latter is a product of the action of the acid of the seed. This fact is in harmony with experiments described in a former paper of ours on the action of minute quantities of acid on globulins.[1] In very dilute acids and alkalies in absence of salts, legumin dissolves readily and abundantly, from which solutions, if at once neutralized, it is precipitated in a form soluble in sodium chloride solution. By this treatment no evidence of change has been detected. Solutions made with hydrochloric acid are precipitated by a small excess of acid, but those made with acetic acid are not precipitated by any excess of acid.

Solutions of legumin in ten per cent. sodium chloride brine are not rendered turbid by long heating in a boiling water-bath.

Dissolved in ten per cent. sodium chloride brine, legumin is precipitated by a very little hydrochloric acid, but a relatively considerable amount of acetic acid is required to produce a precipitate in such solutions.

Sodium chloride solutions of legumin give large precipitates with tannic acid as well as with picric acid, those formed by the latter dissolving in an excess of salt solution if too much picric acid had not been previously added. With mercuric chloride no precipitate is produced.

With nitric acid, Millon's and Adamkiewicz's tests, proteid reactions are obtained. With the biuret test a violet color is given which on standing becomes a deep rose-red like that given by peptones.

[1] Report of the Connecticut Agricultural Experiment Station for 1896, p. 360. This Journal, 19, 482.

Legumin has been supposed by some investigators to contain phosphorus and therefore to belong with the nucleo-proteids. A careful testing of thoroughly purified samples, by fusing with caustic soda and nitrate, and treating the solution of the fusion acidified with nitric acid with ammonium molybdate, showed that in some of the preparations only just detectable traces of phosphorus were present, while other preparations contained none whatever.

Although we have examined large numbers of our preparations of the different plant proteids for phosphorus, we have as yet found none which, in carefully purified samples, contained more than a few hundredths of a per cent., a quantity so small that it is reasonable to consider it as a constituent of the ever-present ash.

The composition of legumin is shown by the following figures, which are averages of a number of preparations from each of the different seeds:

LEGUMIN.

	Pea.	Lentil.	Horse bean.	Vetch.	Average.
Carbon	51.74	51.73	51.72	51.69	51.72
Hydrogen	6.90	6.89	7.01	6.99	6.95
Nitrogen	18.04	18.06	18.06	18.02	18.04
Sulphur	0.42	0.40	0.39	0.43	0.41
Oxygen	22.90	22.92	22.82	22.87	22.88
	100.00	100.00	100.00	100.00	100.00

VICILIN.

Vicilin is a globulin associated with legumin in the pea, lentil, and horse bean. But as we have no means of separating vicilin and legumin quantitatively, we can state nothing respecting the amount in which it occurs in these seeds further than that the lentil contains the most and the horse bean the least. In the lentil it probably forms about one-third of the mixed globulins. That vicilin is not a derivative of legumin, is almost conclusively proved by the fact that no vicilin can be obtained from the vetch.

The most remarkable characteristic of vicilin is its content of sulphur, less than that of any other known proteid. This element, it may be noticed, diminishes in quantity with repeated

precipitation as though by this process sulphur were split off from the molecule. The total quantity, however, is so small that it might appear unsafe to draw conclusions from the differences observed, that is from 0.23 per cent. maximum to 0.08 per cent. minimum. Yet repeated determinations of this element have shown us that the differences were not analytical. It would seem possible by sufficiently repeated precipitation to obtain from this proteid preparations free from sulphur.

In salt solution vicilin is much more soluble than legumin, so that by repeated precipitation from diluted solutions the two globulins can be separated.

When solutions of vicilin in ten per cent. brine are heated in a water-bath they become turbid at 90° and at 95° flocks separate. When heated for some time at 100° this globulin is almost completely coagulated. In water, vicilin is insoluble. In one per cent. sodium chloride solution it dissolves considerably, while in slightly stronger solutions it is much more soluble, the solution of the globulin appearing to depend on the presence of enough salt to form a soluble compound.

In its other reactions it very closely resembles legumin.

The composition of vicilin we found to be as follows:

VICILIN.

	Pea.	Lentil.	Horse bean.	Average.
Carbon	52.36	52.13	52.38	52.29
Hydrogen	7.03	7.02	7.04	7.03
Nitrogen	17.40	17.38	17.52	17.43
Sulphur	0.18	0.17	0.15	0.17
Oxygen	23.03	23.30	22.91	23.08
	100.00	100.00	100.00	100.00

LEGUMELIN.

We have found legumelin in all the leguminous seeds which we have examined with the exception of the white bean (*Phaseolus vulgaris*) and the blue and yellow lupin.

It is difficult to decide whether this proteid should be considered an albumin or a globulin.

By prolonged dialysis of solutions containing considerable legumelin a very small part separates, usually in a form insoluble in salt solutions. In one case we obtained a precipitate by

dialysis which was wholly soluble in brine, to a solution from which a relatively large coagulum separated on heating to 65°, thus indicating a globulin. We have found, however, that other proteids, notably edestin, undergo a change in solubility, whereby the proteid becomes gradually more and more difficult to dissolve. Thus edestin changes from a form insoluble in cold brine to one soluble in hot brine, also from one soluble in hot brine to one insoluble therein, but soluble in dilute sodium carbonate solution, and finally from a form insoluble in alkali carbonate to one soluble only in caustic alkali. It is not unreasonable to expect that a proteid which might properly be considered an albumin (*i. e.*, soluble in pure water and coagulable on heating) should undergo a similar change whereby it becomes no longer soluble in pure water but dissolves in salt solutions and then further changes to a form no longer soluble in brine but dissolved by alkali carbonates.

Such a very large proportion of the legumelin resists precipitation by dialysis, that we are inclined to regard the small precipitates which we have obtained in this way as due to changes similar to those which produce so-called "albuminates" from globulins.

In a paper on the proteids of the cow pea we designated this proteid as a globulin, but in view of our subsequent, much more extensive experience we now consider legumelin to be more properly classed with the albumins.

The amount of legumelin which we have found in the seeds discussed in this paper, was in the pea two per cent., vetch one and one-half per cent., lentil and horse bean one and one-quarter per cent.

No definite coagulation point can be stated for legumelin, as the presence of salts or acids as well as the proportion of dissolved legumelin have a great effect on the temperature at which coagulation takes place. Coagulated legumelin is soluble in very dilute alkalies, as is shown by the following experiment tried with preparation 41 from the pea. About seven-tenths gram of this substance which had been nearly dried over sulphuric acid, but which still contained some alcohol, was suspended in fifty cc. of water and ten cc. of one-half per cent. caustic soda solution added. The legumelin dissolved at once,

giving a glairy solution very similar in appearance to undiluted white of egg. After standing a few moments the viscidity disappeared and the solution became thin and clear. This solution was then almost neutralized by adding a nearly sufficient quantity of a dilute acetic acid which had been previously titrated against the soda solution. The liquid still remained clear and the legumelin was not precipitated until but a trace of the alkali remained unneutralized.

In dilute hydrochloric or acetic acid the coagulum is not soluble. By adding ten per cent. of sodium chloride to solutions containing legumelin, and then acetic acid, the acid compound of this proteid is precipitated, which dissolves in water to a solution that on neutralization gives a precipitate insoluble in water.

By saturating seed extracts, freed as far as possible from all globulin, with sodium chloride or magnesium sulphate only a very slight precipitate is obtained, showing that legumelin is thus slightly if at all precipitated.

Owing to the impossibility of separating legumelin from associated proteose, except in a coagulated state, we have learned but little respecting its reactions.

In the following table we give the average of analyses which we have made of coagulated legumelin from different seeds. These preparations have been obtained in a variety of ways, as can be seen by consulting our papers on the seeds named.

LEGUMELIN.

	Pea.	Lentil.	Horse bean.	Vetch.	Adzuki bean.	Cow pea.	Soy bean.	Average.
Carbon	53.31	53.22	53.03	53.31	53.97	53.25	53.06	53.31
Hydrogen ..	6.99	6.82	6.97	6.97	7.01	7.07	6.94	6.97
Nitrogen ...	16.30	16.27	16.22	16.24	16.31	16.36	16.14	16.26
Sulphur....	1.06	0.94	1.30	1.11	0.88	1.11	1.17	1.08
Oxygen	22.34	22.75	22.48	22.37	21.83	22.21	22.69	22.38
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Ritthausen recognized the presence of this proteid in the horse bean and pea, and gave analyses of coagula obtained by boiling extracts of these seeds. These analyses, however, do not agree well with each other and only in a general way with ours. On account of the solubility in alkali of the heat coagulum of this proteid, he did not consider it to be albumin.

PROTEOSE.

As the proteose of these seeds is present in small amount and is difficult to obtain pure, we have not as much information respecting it as is desirable. The pea appears to contain about one per cent., the horse bean about one-half per cent., and the lentil and vetch evidently less. It is probable that more or less of this proteose may be lost by diffusion, for 10.5 grams of what was doubtless nearly pure proteose from the pea, after solution and dialysis yielded only about six grams when reprecipitated. We have obtained a few of the reactions of proteose from the pea and horse bean, but no reactions of this proteid from the lentil and vetch.

By saturation with salt, solutions of the proteose of the pea and horse bean are not precipitated, but by subsequently adding salt saturated acetic acid, a large part of the pea proteose separates while all but a trace of that from the horse bean is thrown down. Nitric acid in the aqueous solutions of the pea proteose gives no precipitate unless the solution is previously saturated with salt, when a precipitate, soluble on warming and reappearing on cooling, is given by that part of the proteose precipitable by acetic acid from a salt saturated solution, while the part not thus precipitable gives only a turbidity. Both these parts of the pea proteose are precipitated by copper sulphate, and give a rose-red biuret reaction.

The composition of the preparations from these seeds was found as follows:

PROTEOSE.

	Pea.		Lentil.	Horse bean.		Vetch.
	46	47	68	89	98	22
Carbon	50.24	49.66	50.17	50.24	49.96	50.85
Hydrogen	6.76	6.78	6.77	6.66	6.76	6.75
Nitrogen	17.35	16.57	16.81	17.11	16.95	16.65
Sulphur	1.25	1.40	1.27	1.87	2.75	25.75
Oxygen	24.40	25.59	23.98	24.12	23.58	
	100.00	100.00	100.00	100.00	100.00	100.00

46, Precipitated by saturating with salt and adding acetic acid.

47, From the filtrate from 46.

68, Total proteose precipitated by alcohol.

89, Ditto.

98, Precipitated from salt saturated solution by acetic acid.

22, Total proteose precipitated by alcohol.

If the difficulty encountered in purifying these preparations of proteose and the different methods by which they have been obtained are considered, the agreement between them, except for the sulphur in those from the horse bean, makes it probable that these figures quite nearly represent the composition of this substance.

PROTEIDS OF THE SOY BEAN.[1] (*Glycine hispida.*)

By Thomas B. Osborne and George F. Campbell.

THE proteids of the soy bean, so far as we are informed, have never been the subject of special investigation. The seeds used by us were grown in Kansas and kindly supplied by Prof. C. C. Georgeson. Two varieties have been examined, one known as the yellow soy bean and the other, called in Japan, *kiyusuki diadzu*.

YELLOW SOY BEAN.

The seeds were first coarsely ground, then freed almost entirely from the outer coats by a current of air and finally ground to a fine flour.

From this meal, water dissolved a large quantity of proteid, yielding an extract exceedingly difficult to filter and impossible to make perfectly clear, for the solutions, even after repeatedly filtering through the densest filters, were always strongly opalescent.

The aqueous extract reacts acid with litmus, about 0.75 gram of caustic potash being required to produce a neutral reaction in an extract from 100 grams of meal. When thus neutralized no noticeable precipitate is produced, indicating the absence of acid proteid compounds. Dilute acids give abundant precipitates in the aqueous extract, as does the addition of lime salts, the precipitates produced by these reagents being readily soluble in sodium chloride solutions.

[1] Reprinted from advance sheets of the Report of the Connecticut Agricultural Experiment Station for 1897. Communicated by the authors.

Dialysis of the aqueous extract of 100 grams of meal precipitated 16.6 grams of globulin, which was largely soluble in brine. The solution filtered from this precipitate began to coagulate on heating to about 55°; after further heating to 80° the coagulum amounted to 1.53 grams. The reactions of the aqueous extract are like those similarly obtained from other leguminous seeds and indicate that the globulin is dissolved by means of the potassium phosphates contained in the seed.

To obtain the proteids soluble in sodium chloride solution, 2000 grams of meal were treated with ten liters of ten per cent. brine, the extract was strained through fine bolting-cloth and the residue squeezed in a screw press. The turbid, gummy extract, measuring about eight liters, was centrifugated until no more solid matter could be removed. The liquid was pumped through a thick bed of filter-paper pulp and yielded a reddish yellow solution, which appeared perfectly clear by transmitted light, but was opaque by reflected light. This extract was saturated with ammonium sulphate and a very bulky precipitate obtained which, after draining on filters over night, measured, when removed from the papers, over two liters. This precipitate was stirred up with a little water, strained through bolting-cloth to break up lumps, and dialyzed in running water over night. By this process the excess of ammonium sulphate, which had prevented solution, was so far removed that the proteid completely dissolved with the help of the remaining sulphate, in about three liters of water. The liquid was then filtered perfectly clear and again dialyzed for four days. The contents of the dialyzers were then allowed to deposit the large precipitate of globulin that had separated, and from this the solution A was siphoned off. The precipitate was collected on several filters, the contents of one were thoroughly washed in succession with water, alcohol, absolute alcohol, and ether, and dried over sulphuric acid. Preparation 1, weighing 25.11 grams, was thus obtained. The rest of the globulin was allowed to drain thoroughly on the filters and then dissolved in 750 cc. of five per cent. brine, yielding 1250 cc. of solution. To this was added 1000 cc. of water and the large precipitate produced, after standing about four hours, was filtered out and without washing was treated with ten per cent. brine. Nearly all dissolved, but a very slimy sub-

stance that remained suspended in the solution, made filtration practically impossible. The solution was therefore passed through the centrifugal separator, which removed a small quantity of viscid matter, and was then filtered perfectly clear through paper pulp and dialyzed for two days. The large precipitate which resulted was filtered out and washed with water. The washings at first were clear, but afterwards became turbid in consequence of the precipitation of dissolving proteid. The substance was then washed with dilute alcohol and finally with absolute alcohol and dried over sulphuric acid. This preparation, 2, weighed eighty grams. The aqueous washings of 2 were made clear by adding a little salt and then dialyzed. After two days the precipitate which separated was filtered out, washed with water and with alcohol, giving preparation 3, weighing 5.43 grams. The dialyzed solution from which 2 had separated contained very little proteid. The solution from which 2 had been originally separated by dilution was cooled over night at 7° and decanted from the precipitate that resulted, which formed a transparent layer of thick viscid fluid, as does legumin under similar conditions. This substance was treated with water, which rendered it opaque with separation of a white solid. After thoroughly washing with water the latter was dehydrated with absolute alcohol and dried over sulphuric acid, giving twenty grams of preparation 4. The solution decanted from 4, measuring 1650 cc., was treated with 2000 cc. of water, and after standing at rest for about five hours, was poured off from a semifluid deposit. This, after thoroughly washing with water and alcohol and drying, gave 18.76 grams of preparation 5.

The solution decanted from 5 was cooled to 5° for about eighteen hours, but as very little proteid separated, it was dialyzed for two days and then filtered from a small precipitate. The latter, washed with water and alcohol and dried over sulphuric acid, gave 5.37 grams of preparation 6.

A part of preparation 2 was mixed with five-tenths per cent. sodium carbonate solution, in which it was mostly soluble, and the resulting solution was neutralized with dilute acetic acid. Crystallized salt was then added, whereby the neutralization precipitate partially redissolved. The insoluble substance was filtered out and the clear filtrate dialyzed for forty-eight hours.

The proteid separated in spheroidal form and was filtered out, washed with water and with alcohol, making preparation 7.

A portion of preparation 4 was suspended in water and mostly dissolved by help of a little acetic acid. Dilute sodium carbonate solution was added until the proteid appeared to be completely precipitated, leaving the liquid distinctly acid to litmus. Crystallized salt was added, which gave a nearly complete solution of the precipitate. The solution was filtered and dialyzed for four days, when the precipitated globulin was filtered out, washed, and dried, giving preparation 8.

Another preparation was made from a neutralized extract, by treating 200 grams of meal with two liters of five per cent. salt solution to which had been added a quantity of baryta, previously determined to be sufficient to make the resulting extract neutral to litmus.

The mixture was strained through fine bolting-cloth and allowed to settle over night, but the suspended matter separated very imperfectly. The extract was then filtered on a pulp-filter with a pump, and 1500 cc. of a very nearly clear solution obtained, which was much less opalescent than any previously made from unneutralized extracts. This was saturated with ammonium sulphate and the resulting precipitate dissolved in water; the solution obtained was filtered perfectly clear and dialyzed for three days. The contents of the dialyzer were then filtered and the precipitate was washed with water. A portion of this substance was used to determine the reactions of this proteid and the remainder was washed with alcohol and dried, forming preparation 9.

All the preparations thus described were then dried to constant weight at 110° and analyzed with the following results:

GLYCININ: GLOBULIN OF YELLOW SOY BEAN.

	1	2	3	4	5
Carbon	52.04	51.73	51.84	51.94	51.90
Hydrogen	7.06	6.74	6.89	6.93	7.03
Nitrogen	17.14	17.72	17.46	17.52	17.44
Sulphur	0.77	0.76	0.79	0.73	0.66
Oxygen	22.99	23.05	23.02	22.88	22.97
	100.00	100.00	100.00	100.00	100.00
Ash	0.34	0.57	0.43	0.53	0.41

	6	7	8	9	Average
Carbon	51.75	51.65	51.71	52.12	51.85
Hydrogen	6.90	6.97	6.82	6.93	6.92
Nitrogen	17.03	17.63	17.57	17.53	17.45
Sulphur	0.67	0.66	0.61	0.79	0.72
Oxygen	23.65	23.09	23.29	22.63	23.06
	100.00	100.00	100.00	100.00	100.00
Ash	0.30	1.34	0.61	0.38	....

With the exception of the figures for nitrogen in the crude globulin, 1, and in the final small fraction, 6, these analyses are in close accord and give no evidence of any fractional separation. It is probable, therefore, that we have here a definite proteid distinct from legumin, containing one-half per cent. less nitrogen and three-tenths per cent. more sulphur than that substance. We propose for this globulin the name *Glycinin*. Its reactions, determined by an examination of preparation 9, are as follows:

In sodium chloride solutions it is readily soluble and is precipitated by dialysis, by dilution, and by cooling.

By dialysis or by cooling it separates in the form of spheroids which, according to circumstances, after settling from the solution either unite to a more or less coherent mass or else form a clear, transparent, viscid fluid, which, like legumin under similar conditions, is rendered white and solid by treating with water.

Solutions containing more than two per cent. of sodium chloride dissolve glycinin freely; the solvent power of those containing less salt diminishes more rapidly than the percentage of salt decreases.

Dissolved in sodium chloride solution, glycinin is not precipitated by saturating with magnesium sulphate or sodium chloride, but is completely precipitated by saturating with sodium sulphate at 34°.

In pure water, glycinin, when prepared from carefully neutralized extracts, is not soluble.

If soy bean meal is treated with water, upwards of sixteen per cent. of this globulin is dissolved, but in this case the solution is doubtless due to the potassium phosphates contained in the seed, as was pointed out in our paper on legumin.

Dissolved in ten per cent. sodium chloride solution, glycinin

is not coagulated even by prolonged heating in a boiling water-bath.

By dilute acetic acid a precipitate is formed insoluble in excess of salt solution. If, however, glycinin be dissolved in a solution containing but little salt, the precipitate produced by acetic acid is soluble in a slight excess of either acid or salt. The insoluble, so-called albuminate form of this globulin, like that of legumin, when treated with salt solution becomes gelatinous and it is impossible to filter solutions containing even a small quantity of it.

In absence of salts, glycinin is readily soluble in quite dilute acetic acid and is precipitated from such solution by sodium carbonate, even before the acid is wholly neutralized. When the acid is completely neutralized the precipitate obtained is entirely soluble in brine. Dissolved in ten per cent sodium chloride solution, glycinin is precipitated by tannic acid and by picric acid, the latter yielding a precipitate soluble in an excess of salt solution if too much picric acid be not present. With mercuric chloride no precipitate is produced. With Millon's Adamkiewicz's, the biuret and xanthoproteic test the usual proteid reactions result.

The solution A, page 420, which, as described, had been filtered from the globulin precipitated by dialyzing the solution of the ammonium sulphate precipitate of the total proteids of the extract, contained the remaining proteids extracted from the beans. This solution was saturated with ammonium sulphate, the precipitate so produced was filtered out and dissolved in a small quantity of water. After filtering clear, the solution was dialyzed for eight days. The globulin, which separated in well-formed spheroids, when washed and dried weighed twenty grams, preparation 10. The filtrate from 10 was saturated with ammonium sulphate, the precipitate dissolved in a little water, filtered clear, and dialyzed for five days; a small deposit appeared which when washed and dried weighed 2.71 grams, preparation 11. The solution filtered from 11 was returned to the dialyzer and, as nothing more separated after forty-eight hours, the dialyzer was transferred to alcohol. During the next forty-eight hours a considerable precipitate formed which when washed with alcohol and dried weighed 11.5 grams. Of this

substance seven and five-tenths grams were treated with water and the insoluble part was thoroughly washed with water and alcohol and dried. Preparation 12 was thus obtained, weighing four and seven-tenths grams. The filtrate, from the precipitation of this substance by dialysis in alcohol, was mixed with a large excess of alcohol and the precipitate caused thereby was filtered out, dehydrated with absolute alcohol, dried and found to weigh one and four-tenths grams, preparation 13. These preparations were dried at 110° and analyzed with the following results :

	10	11	12	13
Carbon	51.94	52.00	53.06	48.76
Hydrogen	6.88	6.83	6.94	6.28
Nitrogen	16.51	16.36	16.14	16.14
Sulphur	0.60	24.81	1.17	28.82
Oxygen	24.07		22.69	
	100.00	100.00	100.00	100.00
Ash	0.39	0.19	0.44	1.35

Of these preparations 10 and 11 have nearly the composition of phaseolin, but whether they are identical with that globulin could not be ascertained because they had become so largely coagulated by washing with alcohol and drying, that their reactions could not be satisfactorily determined.

A small quantity of globulin was obtained by further dialyzing the filtrate from preparation 9, page 422, which, when dissolved in ten per cent. salt solution, became turbid at about 95°, and after continued heating at 99°, gave a considerable coagulum. Hydrochloric or acetic acid added to its solution in ten per cent. brine gave no precipitate, and dilution with water gave a precipitate only when carried to a great extent. These reactions are characteristic of phaseolin, and taken in connection with the analyses of the similarly obtained preparations 10 and 11, make it probable that these seeds contain a small proportion of phaseolin.

Preparation 12 has the composition of legumin, which we have obtained in the same manner from a number of other leguminous seeds.

Preparation 13 is proteose.

SOY BEAN. (*Kîyusuki Diadzu.*)

Fine flour made from this variety of the soy bean was first treated with petroleum benzine and obtained nearly free from fat. By extracting 2000 grams of the flour, thus prepared, with brine and proceeding in exactly the same manner as in making preparation 1 from the yellow soy bean, a large precipitate of globulin was obtained, a part of which, when washed and dried, gave preparation 14, weighing twenty-five grams. The remainder of the globulin was drained on filters, suspended in water and 300 cc. of ten per cent. sodium chloride solution added, bringing the volume to 1000 cc. Under this treatment very nearly all dissolved. An equal volume of water was then added to the solution and the separated globulin allowed to settle. The precipitate was collected on a filter and redissolved in ten per cent. brine. The solution was filtered perfectly clear and dialyzed for forty-eight hours. The precipitate, so separated, was washed with water and with alcohol and dried, giving preparation 15, weighing 83.5 grams. The solution filtered from the first precipitation of 15, caused by dilution, as just described, was cooled to 8° during twenty-four hours. The substance thus separated, which formed a clear semifluid layer at the bottom of the jar, was thoroughly washed with water and with alcohol and dried. It weighed 12.85 grams and formed preparation 16.

After drying at 110° to constant weight these preparations were analyzed as follows:

GLYCININ.

	14	15	16	Average.
Carbon	51.80	52.15	52.09	52.01
Hydrogen	6.93	6.87	6.86	6.89
Nitrogen	17.45	17.48	17.47	17.47
Sulphur	0.75	0.72	0.70	0.72
Oxygen	23.07	22.78	22.88	22.91
	100.00	100.00	100.00	100.00
Ash	0.39	0.42	0.28	

These results agree well with those obtained from the yellow soy bean.

GLYCININ.

	Yellow Soy bean.	*Kiyusuki diadzu* Soy bean.
Carbon	51.85	52.01
Hydrogen	6.92	6.89
Nitrogen	17.45	17.47
Sulphur	0.72	0.72
Oxygen	23.06	22.91
	100.00	100.00

CONCLUSION.

The soy bean contains as its chief proteid constituent *glycinin*, a globulin similar in properties to legumin, but of somewhat different composition, containing nearly twice as much sulphur, four-tenths per cent. more carbon, and one-half per cent. less nitrogen.

We give as the composition of this proteid the results of our analysis of preparation 9, which was obtained from a neutral and perfectly clear extract, for we believe that this represents more accurately the true composition of glycinin than the average of all the preparations.

GLYCININ.

Carbon	52.12
Hydrogen	6.93
Nitrogen	17.53
Sulphur	0.79
Oxygen	22.63
	100.00

The soy bean contains a more soluble globulin which resembles phaseolin in composition, and, so far as we could ascertain, also in its reactions. The amount of this proteid is small and the evidence that it is in reality phaseolin was not wholly satisfactory.

Besides these globulins about one and five-tenths per cent. of the albumin-like proteid *legumelin* was obtained. We have found legumelin in a number of other leguminous seeds, the pea, vetch, horse bean, lentil, adzuki bean, and cow pea. The properties of legumelin are given in our papers on "The Proteids of the Pea, Lentil, Horse Bean, and Vetch."[1] The composition of legumelin as found in the soy bean is as follows:

[1] This Journal, 20, 410.

LEGUMELIN.

Carbon	53.06
Hydrogen	6.94
Nitrogen	16.14
Sulphur	1.17
Oxygen	22.69
	100.00

A small quantity of proteose was also obtained from the soy bean having the following composition:

PROTEOSE.

Carbon	48.76
Hydrogen	6.28
Nitrogen	16.14
Sulphur } Oxygen }	28.82
	100.00

Owing to the small amount of proteose no evidence was obtained as to the purity or individuality of this preparation.

ELECTRICAL DISTURBANCE IN WEIGHING.

BY H. K. MILLER.

Received February 28, 1898.

WHILE making some fat determinations, I found a practice, which I believe is quite common among chemists, to be the source of quite serious errors. The practice is that of wiping a flask with a dry cloth just previous to weighing it. In making a second weighing of a flask containing an oil which had been extracted from a sample, I was very much surprised to find a considerable increase over the weight first obtained.

The first idea that presented itself was that the oil had suffered oxidation during the second heating, but this idea was dispelled when to my greater surprise a third weighing showed the flask and contents to weigh even less than at first. Careful experiments led to the conclusion that in wiping the flask it became electrified, and that this static charge, acting on the floor of the balance, induced on it a charge of opposite character, and that the mutual attraction between these two charges of electricity had the effect of apparently increasing the weight of the flask.

The potential of the charge would vary with the atmospheric conditions and with the manner of wiping the flask. By using a linen cloth in very dry weather, it was found possible to produce a charge on a 100 cc.-flask which would require 0.08 gram additional weight to restore equilibrium.

A high charge like this, however, would be rapidly dissipated and the flask would appear to lose weight. It was found that a charge which apparently caused an increase in weight of about 0.01 gram would be retained quite a long time, and one might readily overlook the error which would be thus introduced. It was further found that a small charge would be retained many days on a flask kept in a desiccator. In damp weather a charge would readily pass off and not give rise to an error, but on a very dry day the practice of wiping glassware just before weighing is liable to cause serious errors.

ANALYTICAL NOTES UPON THE ESTIMATION OF PHOSPHORUS IN STEEL.[1]

BY R. W. MAHON.

Received March 4, 1898.

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[1] In this paper I have recorded a number of experiments upon the estimation of phosphorus in steel. Their subject is a study in detail of the molybdate-magnesia method. Some of the experiments are upon properties of the molybdate precipitate, which are not connected with this method for estimating phosphorus. The concluding pages describe precipitation of phosphoric acid, out of measured quantities of a standard solution of sodium phosphate.

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THESE experiments were made with steel of low carbon content (below 0.10). The preparation of the solutions of the steel for the molybdate precipitation applies to soft steel. The remainder is of general application in steel analysis. These steels do not contain arsenic, and I have not considered the separation of arsenic and phosphorus, except incidentally.

THE SAMPLES.

A volume of liquid steel is throughout of practically uniform composition, and the percentage of phosphorus in all parts of it is the same.

LADLE TESTS FROM A TWENTY THOUSAND POUNDS HEAT OF BESSEMER STEEL, WHICH WAS POURED INTO THREE MOLDS.

Test number.	Percentage of phosphorus.	Remarks.
1.....	0.096 (average)	Sample taken as the steel was about to be poured into the second mold.
2.....	0.100 "	About to be poured into the third mold.
3.....	0.098 "	Third mold nearly full.
1.....	0.098	Another example.
2.....	0.102	
3.....	0.102	
4.....	0.102	

On the other hand, it is sometimes difficult to obtain drillings from a billet or finished shape, which accurately represent the composition. Incorrect opinions have doubtless been drawn of the relation between physical properties and chemical composition, and also with regard to the accuracy of methods, from neglect to remember the facts of segregation. The four samples of steel employed in this work were planed from the surface of billets, rejecting the first portion. The planings from sample No. 1 were mixed and bottled. The others were prepared as follows: The planings were sieved in a coffee strainer, the

dust rejected, and the remainder mixed and bottled. The dust for each was about one-twenty-sixth of the whole. Estimations of phosphorus in drillings, made at about twelve places on the surface of the billet from which sample No. 1 was planed, showed that segregation had taken place to a limited extent.

ESTIMATIONS OF PHOSPHORUS IN THE DUST AND COARSER PARTICLES.

Sample number.	Percentage of phosphorus. Coarser planings, average.	The dust, average.
2	0.103	0.109
3	0.101	0.100
4	0.108	0.111

The determinations in different parts of the fluid mass, and in the particles of different size planed from billet surfaces, were made by titration of ammonium phosphomolybdate with potash solution. As the point of the plane passes over a portion of the surface at which phosphorus has segregated, more dust is formed than from the remainder of the surface, which is softer and less brittle, and the dust sifted out will be higher in phosphorus, if there is segregation upon the surface. That the more brittle portions of a surface will yield the larger proportion of dust is evident; it has also been referred to by Von Jüptner[1], who quotes experiments of Leopold Schneider.

In spite of slight segregation on some of the surfaces from which samples were planed, they are regarded as fairly uniform owing to their subsequent treatment. This applies to all of the samples but No. 1. I have been able to use some of the results from No. 1, but not all. Continued tilting of the jar containing the sample, concentrated the dust at the bottom. Removal of the fine portion would not appreciably change the percentage of phosphorus, but concentration to three times the original amount would raise the percentage of phosphorus 0.001 per cent., assuming that the phosphorus in both coarse and fine portions for samples Nos. 1 and 2 are the same, both having been planed from the same face.

PROOF FOR ACCURACY OF PROCESS.

After obtaining a solution of the sample in nitric acid and oxidizing it, it is possible to determine the accuracy of the steps in the molybdate-magnesia method, by carrying the pyro-

[1] Oest. Zeit. Berg u. Hütten., xiv, 159, per *J. Iron and Steel Inst.*, *1896*, No. 2, 439.

phosphate again through the cycle of operations which were performed in the analysis. I have done this and recorded the results in the following table. Each weight of magnesium pyrophosphate used to calculate a percentage of phosphorus mentioned in the table was corrected by fusing with alkaline carbonates, extracting with water and acid, and evaporating to dryness, taking up with acid, and filtering. The residue was the correction, and the filtrate was used for the reprecipitation of ammonium phosphomolybdate. This method of correcting the weight is not the best way, giving corrections slightly too small. It is also unnecessarily tedious. It was used in these few experiments in order to reconvert pyrophosphate into orthophosphate. The carbonates were examined for phosphorus with negative results.

Results Nos. 1, 2, and 3, of column 3, were obtained by titrating ammonium phosphomolybdate precipitates which had been washed with cold water, with potash solution. The precipitates were thrown down from the solution of the orthophosphate obtained as described above. Its acid solution was rendered alkaline by ammonia and then acid by nitric acid, and molybdate solution added at proper temperature. Although these results were satisfactory, others were obtained in which the large quantity of the salts of the fixed alkalies appeared to interfere with success. I therefore performed the experiments of which the results are recorded in the 4th, 5th, and 6th places of column 3. Here each solution was treated with ferric chloride[1] and after a basic acetate precipitation, a solution was prepared from the precipitate by solution in hydrochloric acid which was then employed for the molybdate precipitation after neutralization as in the previous examples. These later molybdate precipitations were always satisfactory. In these also the estimation was made by titration with potash solution. Results 7 and 8, in column 3, were obtained as follows: The weights of magnesium pyrophosphate from which (corrected) the results 7 and 8 of column 2 were calculated, having been fused with alkaline carbonates and solutions prepared from the fusions as described, basic acetate precipitations and then molybdate precipita-

[1] The amount of ferric chloride used was such that a sum of less than 0.0002 per cent. of phosphorus for ten grams of sample was introduced.

tions were made as described for 4, 5, and 6. In the solution of the molybdate precipitate in ammonia, the phosphorus was precipitated as magnesium ammonium phosphate and finally weighed as before as pyrophosphate, finding a correction to be applied for impurity present, as in the first pyrophosphate. The treatment of the solution of the molybdate precipitate in ammonia, for separation of the trace of iron present in the colloidal state, and the adjustment of the other details necessary to accurate precipitation of magnesium ammonium phosphate, both here and for the first precipitate are identical in all essentials with those employed in estimations giving accurate results, recorded in the longer tables. These details will be described.

The following table contains eight determinations of phosphorus in a sample of steel by the molybdate-magnesia method, and eight re-determinations, using the weights of pyrophosphate as starting-points.

Number of the determination.	Percentage of phosphorus by the molybdate-magnesia method.	Redeterminations using the weights of magnesium pyrophosphate as starting-points.	Remarks.
1	0.104	0.103	By precipitation as ammonium phosphomolybdate, out of the solution of the fusion of the phosphate.
2	0.104	0.102	
3	1.102	0.101	
4	0.103	0.103	By the same method as the first three preceded by a precipitation with basic ferric acetate.
5	0.104	0.103	
6	0.103	0.101	
7	0.102	0.101	By the same method as last three, followed by solution in ammonia, and precipitation with magnesia mixture.
8	0.104	0.102	

I have determined the phosphorus frequently in this sample and consider it to be 0.103. The molybdate-magnesia method may be considered as proceeding to its end in the three following steps:

I. OBTAINING A SOLUTION FROM THE STEEL OF AMMONIUM PHOSPHATE CONTAINING ALL THE PHOSPHORUS AND ONLY A FAINT TRACE OF IRON.

The True Percentage of Phosphorus in Steel and the Result of Analysis.—Methods for estimating phosphorus in steel, involving

precipitation as ammonium phosphomolybdate, proceed upon two assumptions: (1) that no phosphorus escapes during solution and (2) that it is all obtained in a precipitable form. It needs only a simple experiment to convince one's self of the fact that nitric acid of 1.135 sp. gr. proposed for use in steel analysis by Drown,[1] dissolves steel without evolution of hydrogen phosphide. I have made such an experiment, and after passing the gases through silver nitrate have made an examination for phosphoric acid with negative result. The nature of the reaction between silver nitrate and hydrogen phosphide is not unknown to us and indeed Von Jüptner[2] has recently familiarized us with it, through his experiments upon a possible difference of the mode of occurrence of phosphorus in steel, using the precipitated silver as a measure of the hydrogen phosphide given off by the action of dilute sulphuric acid on the steel. I have preferred to examine the absorbing solution (after suitable preparation) by the addition of ammonium molybdate.

On the other hand the second assumption upon which the determination of phosphorus in steel rests, namely that all of the phosphorus in the solution of the steel can be obtained in a precipitable form, is not so easy of proof, and indeed in its nature may be regarded as incapable of absolute proof. It can only be affirmed of a given method for preparing a solution of steel for precipitation that it yields the highest percentage of phosphorus, which is obtained by any other procedure. It does not follow that all of the phosphorus in the sample has been obtained. This latter statement could only be made after having made a compound of given content in phosphorus and obtaining the known result by analysis. To complete the proof the compound must have been made in the same manner: in fact it would be steel, and absolutely homogeneous. These are conditions impossible of fulfilment. The statement that all of the phosphorus in the sample had been obtained, could be made only after getting the same result by difference. This presupposes methods for determining the remaining constituents so delicate as to admit of this, a condition to which the art of analysis has not yet attained.

[1] *Trans. Am. Inst. Min. Eng.*, 18, 90.
[2] *J. Iron and Steel Inst.*, 1897, No. 1, 224.

Oxidation.—In preparing a steel for precipitation of its phosphorus, after solution in dilute nitric acid, by oxidation, the various oxidants are of unequal value. The experiments in the following table are not to show the impossibility of oxidizing mild steels by the several means mentioned, but only the relative difficulty when compared with potassium permanganate. It is possible that in most of the cases, perhaps in all, the oxidation would be perfect were the action sufficiently long continued, or a sufficiently large amount of the oxidizer used, or if both these conditions were favorable. In each of the experiments of the table, four grams of steel were boiled in seventy cc. of water and thirty cc. of nitric acid (sp. gr. 1.42). The oxidation in question was then attempted, the solution afterwards made ammoniacal and then just acid by nitric acid, and fifty cc. of molybdate solution added to the solution, which was at 75° C. The precipitates were titrated with potash solution.

THE EFFECT OF VARIOUS OXIDANTS UPON THE DILUTE NITRIC ACID SOLUTION OF A STEEL WHOSE PERCENTAGE OF PHOSPHORUS IS 0.108.

Additional means of oxidation, besides the nitric acid employed for solutions of the sample.	Percentage of phosphorus.	Remarks.
None	0.060	The solution was boiled a short time.
"	0.060	The solution was boiled a short time.
"	0.075	The solution was boiled a long time.
Hydrochloric acid	0.081	The solution boiled, hydrochloric acid
" "	0.085	added and again boiled.
Potassium chlorate	....	A small quantity of the crystals. A very defective precipitation.
Potassium chlorate and hydrochloric acid	0.107	Thirteen grams of crystals. Hydrochloric acid to dissolve precipitated oxides of manganese.
Bromine water	0.073	
" "	0.062	
Sodium peroxide	0.083	A considerable quantity of the solid substance.
Hydrogen dioxide	0.084	A few cc.; strength unknown.
Hydrogen dioxide and hydrochloric acid	0.090	Added alternately in small quantities.
Hydrogen dioxide	0.109	Sixty cc.; a few cc. at each addition.
Chromic acid	0.094	A few cc. of nitric acid, sp. gr. 1.42, saturated with chromic acid.
Potassium bichromate	0.079	A few cc. of water, saturated with potassium bichromate.
Baked on steam-bath for several days at about 80°C.	0.108 0.107	Taken up with hydrochloric acid, and boiled down; then boiled down twice with nitric acid.

Precipitation of Ammonium Phosphomolybdate.—Each of the determinations by the molybdate-magnesia method was made upon ten grams, in two quantities of five grams each. Shimer[1] originally evaporated the solution, after solution of the steel, oxidation by potassium permanganate, and solution of the precipitated oxides in hydrochloric acid, using the filtrate from the silicon determination for phosphorus. The first published reference to the use of hydrochloric acid for dissolving the oxides of manganese, followed without evaporation by neutralization with ammonia, slight acidification with nitric acid and precipitation of ammonium phosphomolybdate, which I have been able to find, is that of H. Wdowiszewski.[2] He was careful to use only a small quantity of hydrochloric acid.

My precipitations were made in two ways: One (A) by dissolving the precipitated oxides of manganese in hydrochloric acid, cooling the solution and adding ammonia until a stiff mush is obtained, then adding nitric acid in excess, and precipitating by adding fifty cc. of molybdate solution to the solution of the steel which is at 75° C. The free acid present expressed as nitric acid of 1.42 sp. gr. in cc., was for this method about thirty cc., half of this being contained in the solution of the steel and half in the molybdate solution added, conditions of precipitation as to precipitant in excess and free acid, far within the limits of safety described by Hundeshagen.[3] I find among the experiments of Fresenius[4] upon this subject, one in which the same result in phosphoric acid, 0.0208 gram, was obtained when precipitating by magnesia mixture directly from a certain volume of sodium phosphate solution, properly prepared as to ammonium chloride content, and with the addition of ammonia; and also after the precipitation as ammonium phosphomolybdate from an equal volume of phosphate solution, redissolving and reprecipitating by magnesia mixture as before. He added fifty cc. of molybdate solution in effecting the precipitation of phosphoric acid, having first added forty cc. of nitric acid of 1.37 sp. gr. Here a perfectly accurate precipitation was made in presence of forty-seven grams of nitric acid (HNO_3). In my (A) precipita-

[1] *Am. Inst. Min. Eng.*, *1888.*
[2] *Stahl und Eisen*, 12, *1892*, 381 per *J. Soc. Chem. Ind.*, *1892*, 845.
[3] *Ztschr. anal. Chem.*, 28, 141.
[4] *Ibid.*, 3, 446.

tions there were approximately thirty grams of nitric acid (HNO_3) present. In (B) fifteen grams approximately.

Fresenius' well-known molybdate solution recipe—molybdic acid one part, ammonia of 0.96 sp. gr. four parts, and nitric acid of 1.20 sp. gr. fifteen parts—is the one used in my experiments; *viz.*, molybdic acid 100 grams, ammonia of 0.90 sp. gr. 200 cc., water 200 cc., and nitric acid of 1.20 sp. gr. 1250 cc.

Slight agitation in unstoppered Erlenmeyer flasks, and standing ten minutes, causes perfect precipitation. Six precipitates, from five grams of steel each, were filtered in ten minutes. These were heated in covered flasks to 75° C. and then allowed to stand at temperature of room, over night. All remained clear. Six others were filtered in ten minutes, and their filtrates heated to 75° C. for eighteen hours, all remaining clear. One precipitate from five grams was filtered in ten minutes, and one in six hours. These two precipitates, when titrated, gave :

	Per cent. of phosphorus.
Precipitate filtered in ten minutes	0.103
" " " six hours	0.103

The other way (B) of precipitating ammonium phosphomolybdate, I have described,[1] suggesting it as available for a rapid method.[2]

According to this way of working, the steel is dissolved and oxidized as before; redissolving the precipitated oxides resulting from the addition of three cc. of a saturated solution of potassium permanganate used for oxidation, with ten cc. of hydrochloric acid 1.20 sp. gr. The precipitation is made almost immediately upon removal from lamp, by pouring a mixture of fifty cc. of molybdate solution and fifteen cc. ammonia of 0.900 sp. gr. into the solution. The precipitation here is even more rapid than by method A.

Note on the Difference in Ammonium Phosphomolybdate Precipitate by Methods A and B.—When ammonium phosphomolybdate is titrated with potash solution, if the precipitate is obtained by method B, the results are slightly higher than when obtained by

[1] This Journal, 19, 792.

[2] I have recently seen for the first time some experiments of Albert Attenberg, *Land. Versuchstat.*, 26, 423, as abstracted in *Ztschr. anal. Chem.*, 21, 568. He added molybdate solution to the solution of the phosphate, and then boiled the mixture with constant stirring. Another device which he suggested for rapid precipitation, was using neutral molybdate solution. His paper gives no results by this latter modification.

method A, as reported in the paper above referred to. This depends on some molybdate being carried down with the precipitate. The cause of this is its rapid formation, enclosing molybdate, and not on account of the precipitation of molybdic acid as such. The precipitation of molybdic acid is seen when the molybdate solution and ammonia mixture is rapidly poured into the solution of the steel, the latter being at a temperature of 105° C., without taking pains to direct the stream into the center. Where it runs down the sides of the flask into the solution, molybdic acid is seen to separate in quantity, and again to go into solution when the flask is agitated, leaving a clear solution, out of which ammonium phosphomolybdate precipitates.

That B gives slightly higher results than A when titrating with potash solution, does not necessarily arise from more molybdate present in the precipitates in the first case. The cause might be, it is possible to imagine, a molecule formed with more free acid content, hydrochloric or nitric, than the two molecules mentioned by Hundeshagen.[1] It can, however, be shown that the difference arises from the first cause, by estimations of phosphorus in a standard steel, using three methods, and employing precipitates formed in both ways.

TABLE EXPLAINING THE DIFFERENCE OF RESULTS BY A AND B.

	By caustic potash.	By weight of precipitate, dried at 110° C.	By potassium permanganate.
A.....	0.108	0.108 0.109	0.109 0.109
B.....	0.110	0.112 0.110	0.112 0.110

The difference in percentage of phosphorus found by direct treatment of molybdate precipitate is not dependent, however, upon the difference in the method of neutralization employed, but upon the temperature of precipitation, as can be proved by precipitating at 105° C. after neutralization in the older way, and after neutralization in the newer way by precipitating at 75° C.

	Temperature of precipitation.	Percentage of phosphorus found.
Old method of neutralization ..	105° C.	0.111
New " " " ..	75° C.	0.108

[1] *Loc. cit.*

WASHING AMMONIUM PHOSPHOMOLYBDATE.

Number.	Percentage of phosphorus found.	True percentage of phosphorus.	Method of precipitation.	The washing.
1	0.107	0.108	A	850 cc. of cold water.
2	0.105	0.108	A	850 cc. " " "
3	0.107	0.110	B	1000 cc. " " "
4	0.107	0.110	B	1000 cc. " " "
5	0.062	0.108	A	1125 cc. " two per cent. nitric acid.
6	0.039	0.108	A	1125 cc. " two per cent. nitric acid and then with 110 cc. of cold water.
7	0.097	0.110	B	75 cc. of cold water, then 1000 cc. of two per cent. nitric acid, then 200 cc. cold water.
8	0.091	0.110	B	225 cc. of cold water, then 1000 cc. of two per cent. nitric acid, then 300 cc. cold water.
9	0.108	0.108	A	200 cc. of two per cent. nitric acid, then 75 cc. cold water.

These were made with the same sample, and 0.108 and 0.110 denote the results of accurate determinations when titrating precipitates obtained by methods A and B respectively.

Isbert and Stutzer[1] first used cold water to wash the molybdate precipitate. Their results show no loss when washing with 500 cc., and but a slight loss when one liter is used. See Nos. 1 to 4 inclusive, in which the results are slightly lower than those obtained by washing with one-fifth or one-fourth of the mentioned quantities, as in an actual estimation. It was only in preparing precipitates for titration with potash solution that water was the washing fluid.

In dilute nitric acid the molybdate precipitate is much more soluble. (See No. 5.) In this one an empty paper was washed with the same washing fluid, and the result used as a correction.

When a copious washing with nitric acid is followed by a washing with water, the solubility is even more marked; in the latter case being accompanied by a visible running of some of the precipitate through the paper. (See Nos. 6 to 8 inclusive.) These figures are evidently not the result of simple solution, but of decomposition from prolonged washing, a decomposition

[1] *Ztschr. anal. Chem.*, **26**, 584.

rendered more apparent and perhaps increased by subsequently washing with water. Otherwise washing in moderation with dilute nitric acid would dissolve less than in the foregoing examples, but a still appreciable quantity of the precipitate. Actually, washing in moderation with two per cent. nitric acid, does not dissolve any of the precipitate. (See No. 9.) Two hundred cc. of dilute nitric acid is an unnecessarily large quantity to employ.

Re-solution of Molybdate Precipitate.—The absolute separation of small quantities of phosphorus and large quantities of iron by one precipitation of ammonium phosphomolybdate, washing with dilute nitric acid is impossible.

WEIGHTS OF FERRIC OXIDE RETAINED BY THE PRECIPITATE FROM FIVE GRAMS OF STEEL.

Precipitation.		Weights of ferric oxide.
A	1	0.0016
	2	0.0017
B	1	0.0015
	2	0.0015

This iron present in the colloidal condition in the ammoniacal solution of the molybdate precipitate separating upon evaporation, and carries down with it about two-tenths of a milligram of phosphorus in these steels. It is my custom to filter at this point,[1] redissolve the iron in hydrochloric acid, make its solution ammoniacal, and then faintly acid with nitric acid; now add a few cc. of molybdate solution. The small precipitate having been filtered and redissolved in ammonia, its solution running into the main quantity of ammonium phosphate, this is to be evaporated, until the smell of ammonia has disappeared and the bulk is sufficiently reduced.

The solution is now prepared for precipitation by adding the quantity of hydrochloric acid required for the particular case, and then ammonia from a burette, finally obtaining a faintly ammoniacal solution which is diluted to the volume wished, and magnesia mixture dropped in, with constant stirring, followed by the addition of ammonia in the same manner.[2]

[1] It is impossible to give an intelligible description of experiments upon this theme without mentioning familiar details.

[2] Blair's Chemical Analysis of Iron, First Edition, p. 82, prescribes the addition of strong ammonia, in the proportion of one-fourth of the final volume. Such a solution

II. THE ACCURATE PRECIPITATION OF PHOSPHORUS AS MAGNESIUM AMMONIUM PHOSPHATE.

The use of magnesium chloride, ammonium chloride, and ammonia. The same washing fluid was used throughout: ammonia of 7.25 per cent. (that is, water three volumes, ammonia, sp. gr. 0.90, one volume) unless otherwise mentioned.

Two magnesia mixtures were used. The first was made from magnesia, hydrochloric acid, and ammonia, and the magnesium chloride and ammonium chloride per cc. determined. This mixture is called 1, in the tables. The second magnesia mixture called 2 in the tables, is described on page 51 of "Blair's Chemical Analysis of Iron," first edition. Fifty-eight grams of ammonium chloride in two liters were used instead of the quantity called for by that recipe.

MAGNESIA MIXTURE, CONTAINING ENOUGH AMMONIA TO IMPART A DECIDED ODOR.

	No. 1.	No. 2.
Magnesium Chloride, crystallized	66 grams.	110 grams.
Ammonium Chloride	69 "	58 "
Volume	2 liters.	2 liters.

contains 7.25 per cent. of free ammonia (NH_3). This is the amount of ammonia added in each of the following experiments, unless otherwise mentioned. Two and five-tenths per cent. of free ammonia (NH_3) in solution and for wash is probably most used for this precipitate—Fresenius' Quantitative Analysis; Fresenius: *Ztschr. anal. Chem.*, 6, 403; Wagner and his coworkers: *Ibid* 19, 444 and 21, 353; etc. It is the strength used in the official method for agricultural analysis in Germany, and is described in Bulletin 46, U. S. Department of Agriculture as part of the official method for agricultural analysis in this country.

THE USE OF MAGNESIUM CHLORIDE, AMMONIUM CHLORIDE, AND AMMONIA.

Number of the estimation.	Sample number.	Percentage of phosphorus.	Magnesium chloride added. Gram.	Ammonium chloride present. Grams.	Ammonium chloride present per cc. Gram.	Volume of precipitation.	Volume of washing fluid.	Magnesia mixture used.	Remarks.
1	1	0.104	0.043	0.57	0.010	60	125	1	
2	1	0.103	0.043	0.57	0.007	76	120	1	
3	1	0.102	0.043	1.07	0.014	76	120	1	
4	1	0.104	0.043	1.42	0.019	76	90	1	
5	3	0.100	0.086	1.14	0.021	54	128	1	
6	3	0.101	0.086	1.14	0.018	62	128	1	Magnesium chloride in small excess. Small quantity of ammonium chloride present.
7	3	0.101	0.086	1.14	0.017	69	126	1	
8	3	0.099	0.058	0.99	0.016	60	105	1	
9	3	0.100	0.086	1.14	0.019	60	130	1	
10	3	0.103	0.086	1.14	0.019	60	125	1	
11	3	0.100	0.058	0.99	0.016	60	130	1	
12	4	0.108	0.077	0.70	0.023	30	110	2	
13	4	0.108	0.077	0.70	0.008	87	100	2	
14	4	0.114	0.090	0.10	0.002	60	120	2	
15	4	0.117	0.090	0.10	0.002	60	120	2	
16	1	0.103	0.043	9.57	0.124	77	98	1	
17	1	0.101	0.043	5.92	0.099	60	130	1	
18	1	0.103	0.043	5.92	0.099	60	130	1	
19	1	0.102	0.043	5.92	0.099	60	130	1	
20	1	0.104	0.043	5.92	0.099	60	130	1	
21	1	0.104	0.043	5.91	0.089	67	130	1	
22	2	0.102	0.043	6.25	0.142	60	112	1	Magnesium chloride in small excess. Moderate quantity of ammonium chloride present.
23	2	0.101	0.043	6.25	0.142	60	112	1	
24	2	0.102	0.043	6.25	0.142	60	112	1	
25	3	0.100	0.086	5.15	0.067	77	147	1	
26	3	0.100	0.086	5.15	0.067	77	144	1	
27	3	0.100	0.058	11.00	0.138	80	120	1	
28	3	0.099	0.058	11.00	0.130	80	130	1	
29	4	0.106	0.077	10.79	0.135	80	100	2	
30	4	0.109	0.077	10.79	0.124	87	138	2	
31	4	0.109	0.077	25.79	0.143	180	110	2	Magnesium chloride in small excess. Large quantity of ammonium chloride present.
32	4	0.109	0.077	25.79	0.143	180	110	2	
33	4	0.116	0.255	1.00	0.025	41	110	2	Magnesium chloride in large excess. Small quantity of ammonium chloride present.
34	4	0.111	0.180	1.65	0.025	57	110	1	
35	4	0.111	0.180	1.65	0.025	60	110	1	

36	4	0.114	0.255	10.00	0.105	95	110	2	Magnesium chloride in large excess. Moderate quantity of ammonium chloride present.
37	4	0.110	0.255	10.00	0.097	103	110	2	
38	3	0.100	0.180	10.18	0.087	117	137	1	
39	3	0.103	0.180	10.18	0.085	120	115	1	
40	3	0.103	0.180	11.00	0.103	107	108	1	
41	3	0.099	0.180	11.00	0.103	107	118	1	
42	4	0.110	0.255	25.00	0.170	153	140	2	Magnesium chloride in large excess. Large quantity of ammonium chloride present.
43	4	0.110	0.255	25.00	0.170	153	140	2	
44	2	0.104	0.130	6.00	0.081	74	90	1	Use of ammonia of 2.5 per cent. in solution of customary size.
45	2	0.102	0.130	6.00	0.090	67	90	1	
46	2	0.104	0.130	6.00	0.090	67	90	1	
47	4	0.101	0.077	20.00	0.070	288	115	2	Large volume for precipitation. Percentage of ammonia 2.5
48	4	0.111	0.077	0.80	0.003	288	110	2	
49	4	0.105	0.281	20.00	0.070	288	115	2	
50	4	0.112	0.077	0.80	0.003	288	110	2	Large volume for precipitation.
51	4	0.119	0.077	0.80	0.003	288	110	2	
52	4	0.111	0.077	10.00	0.035	288	100	2	
53	4	0.105	0.077	10.00	0.035	288	100	2	
54	1	0.098	0.043	25.00	0.104	240	100	1	
55	1	0.100	0.043	25.00	0.104	240	100	1	
56	4	0.101	0.077	20.00	0.070	288	77	2	
57	4	0.103	0.077	20.00	0.070	288	117	2	
58	4	0.110	0.255	10.00	0.035	288	100	2	
59	4	0.111	0.255	10.00	0.035	288	100	2	
60	4	0.105	0.255	20.00	0.070	288	92	2	
61	4	0.106	0.255	20.00	0.070	288	72	2	
62	4	0.109	0.077	5.00	0.083	60	110	2	Magnesium chloride added somewhat slower than heretofore.
63	4	0.107	0.077	5.00	0.083	60	125	2	
64	4	0.111	0.077	5.00	0.083	60	110	2	
65	4	0.107	0.306	6.00	0.084	71	155	2	
66	4	0.107	0.306	6.00	0.084	71	125	2	
67	4	0.107	0.077	5.60	0.093	60	140	2	Magnesium chloride added as in last five. Time of precipitation, 67 and 68—2 hours, 69 and 70—1 hour.
68	4	0.107	0.077	5.60	0.093	60	140	2	
69	4	0.110	0.306	5.90	0.077	77	130	2	
70	4	0.110	0.306	5.90	0.077	77	130	2	
71	.	0.0014	0.043	6.00	.....	60	150	.	Precipitated in 30 minutes.
72	.	0.0032	0.043	6.00	.....	60	165	.	
73	.	0.0026	0.043	6.00	.....	60	170	.	
74	.	0.0024	0.043	6.00	.....	60	110	.	Precipitated in 1 hour.
75	.	0.0014	0.043	6.00	.....	60	110	.	
76	.	0.0026	0.043	6.00	.....	60	110	.	

When magnesium chloride is used in small excess, the result is practically the same, whether ammonium chloride be present in small, moderate, or large quantity. Thus for samples Nos. 1, 3, and 4, the means are:

1.	3.	4.	Sample number.
0.1033	0.1006	0.1080[1]	Small quantity of ammonium chloride present.
0.1028	0.0998	0.1075	Moderate " " " " "
.....	.....	0.1090	Large " " " " "

Error can however occur when using magnesium chloride in small excess if the amount of ammonium chloride be sufficiently reduced. Estimations Nos. 14 and 15, on sample No. 4, show 0.114 and 0.117.

When magnesium chloride is added in large excess error is more frequently introduced. Thus for samples Nos. 3 and 4, the means are:

3.	4.	Sample number.
.....	0.1127	Small quantity of ammonium chloride present.
0.1013	0.1120	Moderate " " " " "
.....	0.1100	Large " " " " "

The figures above for sample No. 4 also show the lessening of plus error brought about by the presence of ammonium chloride in proper quantity.

The larger the excess of magnesium chloride the more rapid the precipitation, and the more ammonium chloride present the slower the precipitation. As too great rapidity causes inaccuracy, and as ammonium chloride solution has a solvent action upon magnesium ammmonium phosphate, it follows that these ingredients must be adjusted within certain limits. In other words, the proper amount of ammonium chloride is dependent upon the excess of magnesium chloride used. That the same amount of ammonium chloride does not prevent plus error irrespective of the excess of magnesium chloride is illustrated by estimation Nos. 36 to 41. Nos. 36 and 37 give a mean of 0.112 instead of the true percentage 0.108. Nos. 38 to 41 inclusive give a mean of 0.101 instead of 0.100. Here the amounts of ammonium chloride are nearly equal, and the magnesium chloride in excess, much greater for Nos. 36 and 37. All the results thus far discussed will be seen by a reference to

[1] Nos. 14 and 15 are not included.

the table to have been obtained when precipitating in solutions of customary size. Estimations Nos. 50 to 61 inclusive were made, effecting the precipitation in large solution. These estimations include examples with small and large excess of magnesia mixture, in presence of ammonium chloride in varied amount. Although useless as suggestions for analysis, they are interesting as showing the variations caused by variations in magnesium chloride and ammonium chloride. Detailed comment is unnecessary; the dissolving effect of ammonium chloride is a chief feature, increasing with the concentration, and lessening with the excess of magnesium chloride. By an exact balance, accurate results would be obtained. But this is uncertain of attainment, and in the twelve examples considered, has not been reached in one. Either the ammonium salt solution was too concentrated for the excess of magnesia and some weight of precipitate was dissolved or the concentration of ammonium salt solution was too slight and the precipitate was contaminated by the excess of the precipitant.

Indeed in Nos. 52 and 53, supposed to be executed identically, accidental variation has caused one to fall above and the other below the truth.

	Percentage of phosphorus.
No. 52	0.111
" 53	0.105
True percentage	0.108

Comparisons of Nos. 50 and 51 with No. 13, and then with Nos. 14 and 15 show that it is not the weight alone, but also the concentration of the solution of ammonium chloride which prevents coprecipitation of magnesia.

Number of the estimation.	Percentage of phosphorus.	Ammonium chloride present. Gram.	Ammonium chloride per cc. Gram.
50	0.112	0.80	0.003
51	0.119	0.80	0.003
13	0.108	0.70	0.008
14	0.114	0.10	0.002
15	0.117	0.10	0.002

In the estimations thus far and in those to be described, the filtrate and wash-water was examined for phosphoric acid, usually only with the finding of traces (less than 0.001 per cent. phosphorus), unless experiments had been made in similar

cases, showing this to be unnecessary. The method was: boiling down until ammonia was driven off, acidifying and adding a few cc. of molybdate solution. One-tenth of a milligram of phosphorus can be detected thus, as can be seen by examining a blank, to which this quantity of phosphorus had been added, as sodium phosphate.

The filtrates from some of the twelve just described, were examined for phosphorus, with the following results:

	50	51	57	58	59	60	61
Percentage of phosphorus in the filtrate	0.000	0.000	0.007	0.000	0.000	0.004	0.001

Nos. 44 to 49 inclusive describe estimations, where the percentage of ammonia is two and five-tenths in the solutions for precipitation. Nos. 44, 45, and 46 give a mean of 0.1033; Nos. 22, 23, and 24 give 0.1017. The first slightly higher, on account of greater excess of precipitant, and a lesser concentration of ammonium chloride, and showing no result from lesser strength of ammonia. The latter mean is correct, and the first has a plus error of 0.0016. Approximately the same relations (except that the same strength of ammonia is present in the estimations now to be compared) exist between Nos. 38 to 41 inclusive, and Nos. 27 and 28.

Nos. 47 to 49 inclusive, like Nos. 50 to 61 inclusive, were obtained by precipitating in large volume. The same idea of variations in the amount of precipitant and of ammonium chloride, is carried out here. The results, like the corresponding ones in the other series, show no variations due to difference of strength of ammonia present.

No. 47, 0.101	No. 48, 0.111	No. 49, 0.105
" 56, 0.101	" 50, 0.112	" 60, 0.105

Nos. 62 to 66 inclusive give results obtained by adding magnesia mixture even slower than in previous cases, as follows: something more than the theoretical amount, dropped slowly in as usual and the remainder added in the same manner after an interval.

No average difference between properly made previous determinations, and Nos. 62 to 66 inclusive, is apparent.

The time of precipitation is part of the general subject of use of

magnesium chloride and ammonium chloride, for it depends upon the quantities of those salts present.

Nos. 67 to 70 inclusive illustrate the effect of excess of magnesium chloride in hastening precipitation. While Nos. 67 and 68 are slightly below the true percentage, in Nos. 69 and 70 while perfect precipitation was obtained in one hour, the precipitant was dropped in, apparently, somewhat too rapidly. But the effect of magnesium chloride in hastening and of ammonium chloride in retarding precipitation is a visible result, which I have often observed in carrying out a number of estimations simultaneously, with these details differing. In Nos. 71 to 76 inclusive, I have only recorded the phosphorus found in the filtrates.

III. OBTAINING THE CORRECT WEIGHT OF MAGNESIUM PYROPHOSPHATE.

Eleven cm. filter-paper seems to be preferable to a smaller size, for the magnesium ammonium phosphate filtration, particles of the precipitate being less liable to crawl above its edge. The dangerous operation of drying, and burning the paper separately, should be abandoned, in favor of enfolding the precipitate in its still slightly moist paper, and burning in an inclined crucible without lid. I always use the end of a stout platinum wire to break up the precipitate, after the carbon of the paper is almost consumed. This operation can be so carried out as to give rise to no error. There are always three impurities in the magnesium pyrophosphate. These are silica, ferric oxide, and molybdic acid; the last if the precipitation has been made in presence of molybdic acid. Silica and ferric oxide are best separated by hot, very dilute hydrochloric acid. Every precipitate derived from steel was corrected for these impurities. Their sum is usually a fraction of one milligram. The weight of molybdic acid, after ignition before the blast-lamp, can be neglected.[1]

[1] Drown, in a paper by George E. Thackray, "A Comparison of Recent Phosphorus Determinations in Steel," *Trans. Amer. Inst. Min. Eng.*, October, 1895, describes his method of making two phosphorus determinations, published in the paper. The following is a part of the description: "Dissolve the ammonium magnesium phosphate in hydrochloric acid and into this solution pass sulphuretted hydrogen for three or four hours, the liquid being nearly boiling the greater part of the time. After filtering off the molybdenum sulphide, and any arsenic which may be present, the ammonium magnesium phosphate is again precipitated by ammonia, with the addition of a little more magnesia mixture." Three determinations of phosphorus in sample No. 4, carried out as I describe them, the first precipitate of magnesium ammonium phosphate being redissolved and treated according to the above quotation resulted as follows: 0.109, 0.108, and 0.109.

It is one or two-tenths of a milligram. I have determined molybdic acid in these precipitates, in the filtrate from silica and iron, by precipitating by hydrogen sulphide. Two of these were filtered and weighed on asbestos felt in a Gooch crucible, after drying, proving to be a small, doubtful fraction of one milligram. Other precipitates of this impurity by hydrogen sulphide were simply observed. A solution was prepared from forty milligrams of molybdic acid in a little ammonia, and this diluted to one liter. Portions of this were measured off, acidified with hydrochloric acid and having been diluted, treated with hydrogen sulphide gas. The quantity of molybdic acid in ten cc. of this solution if present in a pyrophosphate after ignition before the blast-lamp, would cause an error of 0.001 per cent. phosphorus for ten grams of steel. Ten cc. of the solution however if precipitated as above, give a precipitate, much greater than any derived from these pyrophosphates.

Another way of studying this subject is shown in the estimations carried out with standard sodium phosphate solution, described further on, where the error arising from presence of molybdic acid in the ignited precipitate is proved to be zero.

I have determined phosphorus twice in sample No. 4 filtering magnesium ammonium phosphate on asbestos felt in a Gooch crucible. These determinations are uncorrected for admixed silica and ferric oxide, and each gave 0.109 per cent. phosphorus.

WASHING MAGNESIUM AMMONIUM PHOSPHATE.

Sample number.	Percentage of phosphorus.	Magnesium chloride added. Gram.	Ammonium chloride present. Grams.	Ammonium chloride present per cc. Gram.	Volume of precipitation.	Volume of washing fluid.	Magnesia mixture used.	Washing fluid.
1	0.103	0.0432	6.00	0.100	60	250	1	7.25 per cent. ammonia.
1	0.103	0.0432	6.00	0.100	60	250	1	
3	0.096	0.0864	1.20	0.017	69	215	1	2.50 per cent. ammonia.
3	0.099	0.0864	1.20	0.017	69	215	1	
4[1]	0.103	0.077	5.00	0.050	100	220	2	9.67 per cent. ammonia having dissolved in 100 cc. 2.50 grams of ammonium nitrate.
4[1]	0.105	0.051	5.00	0.057	87	240	2	

[1] Blair's Chemical Analysis of Iron, First Edition, p. 82.

The varying figures for ammonium chloride and for magnesium chloride are without significance. Although the last two washing fluids show dissolving power on this precipitate, when used in excessive amount, they are satisfactory as customarily employed, as follows:

Number of the estimation.	Sample number.	Percentage of phosphorus.	Magnesium chloride added. Gram.	Ammonium chloride present. Grams.	Ammonium chloride present per cc. Gram.	Volume of precipitation.	Volume of washing fluid.	Percentage of ammonium in solution of precipitation.	Magnesia mixture used.	Washing fluid.
	1	0.104	0.130	6.0	0.10	60	100	7.25	1	
	1	0.101	0.130	6.0	0.10	60	100	7.25	1	
44	2	0.104	0.130	6.0	0.08	74	90	2.50	1	2.5 per cent. ammonia.
45	2	0.102	0.130	6.0	0.09	67	90	2.50	1	
46	2	0.104	0.130	6.0	0.09	67	90	2.50	1	
	1	0.103	0.086	6.0	0.10	60	100	7.25	1	
	1	0.103	0.086	6.0	0.10	60	100	7.25	1	9.67 per cent. ammonia having dissolved
	2	0.103	0.086	6.0	0.11	53	100	7.25	1	in 100 cc. 2.5 grams of
	2	0.101	0.086	6.0	0.10	60	100	7.25	1	ammonium nitrate.
	2	0.103	0.086	6.0	0.09	67	100	7.25	1	

EXPERIMENTS IN ESTIMATING PHOSPHORUS IN SOLUTION OF SODIUM PHOSPHATE.

The solution was prepared from a salt purchased as chemically pure. This was recrystallized, filtered on the suction-pump, and washed once with cold water. The purified salt was dissolved in water and preserved in a ground glass-stoppered bottle, portions of it being filtered as used. Two quantities of twenty cc. each were evaporated to dryness and ignited in a weighed platinum capsule. The weights of phosphorus calculated from the two weights of sodium pyrophosphate obtained were 0.01008 and 0.01008. If these are expressed as percentages of phosphorus obtained by analysis of ten grams of steel, they would be 0.1008 and 0.1006. The following are the determinations of phosphorus in the solution, by precipitation as magnesium ammonium phosphate, using twenty cc. of the filtered solution for each precipitation.

No. 2 magnesium mixture was used in the determinations of the following table, and 7.25 per cent. ammonia for precipitation and washing fluid.

Number of the estimation.	cc. of hydrochloric acid of 1.20 sp. gr.	cc. of magnesia mixture.	Molybdic acid. Gram.	Method of adding magnesia mixture.	Ammonia or magnesia mixture added last.	Volume for precipitation.	Volume of washing fluid.	Weight of magnesium pyrophosphate.	Phosphorus expressed as a percentage for ten grams of steel.
1	8	3	0.61	A	X	60	81	0.0365	0.102
2	7	3	0.61	A	X	60	73	0.0369	0.103
3	7	10	0.61	A	X	67	85	0.0372	0.104
4	7	10	0.61	A	X	67	85	0.0369	0.103
5	7	3	0.00	A	X	60	83	0.0369	0.103
6	7	3	0.00	A	X	60	87	0.0370	0.103
7	7	10	0.00	A	X	67	85	0.0374	0.104
8	7	10	0.61	B	X	60	85	0.0363	0.1011
9	7	10	0.00	B	X	60	90	0.0363	0.1011
10	7	10	0.00	A	X	60	105	0.0381	0.106
11	2	10	0.61	A	X	60	95	0.0373	0.104
12	2	10	0.00	A	X	60	110	0.0382	0.106
13	1	10	0.61	A	X	60	120	0.0387	0.108
14	1	10	0.00	A	X	60	125	0.0434	0.121
15	7	3	0.61	B	Y	73	77	0.0359	0.0999
16	7	10	0.61	B	Y	73	117	0.0357	0.0994
17	7	10	0.61	B	Y	76	85	0.0361	0.1005
18	7	3	0.61	B	Y	76	105	0.0360	0.1002
19	7	10	0.00	B	Y	76	95	0.0357	0.0994
20	7	3	0.00	B	Y	76	95	0.0356	0.0991
21	1	10	0.61	B	Y	76	95	0.0379	0.106
22	1	10	0.00	B	Y	76	95	0.0384	0.107

The approximate weights of molybdic acid given in column 4 of the table were each dissolved in a little ammonia, and added, after filtration, to the phosphate solution. The hydrochloric acid of column 2 was then added, and then gradually ammonia until the solution became ammoniacal. When cold the solutions X were precipitated by the slow addition of magnesia mixture, this being followed by the addition of ammonia of 0.90 sp. gr., one third of the volume of the solution before its addition being dropped in with constant agitation. To the solutions Y the same quantity of ammonia as for X was first added and then the magnesia mixture dropped in.

A and B of the fifth column, denote: A, that the magnesia mixture was slowly dropped into the phosphate solution with constant agitation; B, that the addition of magnesia mixture was made as for A but with intervals of waiting at each half cc.

for the first three cc. added. After the first three cc. the remainder was dropped in continuously. The A additions occupied about one minute each, the B each about one-half hour or more.

In estimating phosphorus in steel by the molybdate-magnesia method, owing to the number of details involved, when separating molybdenum before the final precipitation as magnesium ammonium phosphate, it is difficult to decide whether its removal, in cases uncomplicated by the presence of arsenic, is advantageous or not. Estimations Nos. 1 to 7 inclusive give some light upon this point. Here there is no difference in results whatever, when precipitating with molybdic acid absent, and in presence of 0.61 gram of molybdic acid (approximately the weight present in analyzing steel of about 0.100 per cent. phosphorus, when employing ten grams in an analysis). There is no apparent difference in the results for Nos. 1, 2, 5, and 6, where three cc. of magnesia mixture were used in precipitating, and Nos. 3, 4, and 7, where ten cc. of magnesia mixture were used. This is because the precipitation had largely occurred before the larger excess of magnesium chloride entered the solution. These first seven are slightly too high. Because, although the magnesia mixture was added rather slowly, it was not added slowly enough to entirely eliminate plus error.

As in the first seven, so also in the remaining ones, the several determinations are duplicated, having no molybdic acid present in the solution when making one precipitation and 0.61 gram when making the other precipitation. The true result, as given by the sodium pyrophosphate determinations, being 0.1007, that is, approximately 0.101. Nos. 8 and 9 give this percentage, being results of almost ideal accuracy. The details differ from the first seven only in the rate at which magnesia mixture was dropped in. On the contrary, the rate of dropping in No. 10 was much increased, even over the first seven, and a greater plus error results, than in these.

In examples Nos. 11 to 14 inclusive the effect of decreasing the amount of ammonium chloride is illustrated. By contrasting Nos. 8 and 9 with Nos. 15 to 20 inclusive, the effect of reversing the order of addition of magnesia mixture and ammonia is seen.

	Percentage of phosphorus.
No. 8	0.1011
" 9	0.1011
Mean	0.1011
Sodium pyrophosphate determination 1	0.1008
" " " 2	0.1006
Mean	0.1007
No. 15	0.0999
" 16	0.0994
" 17	0.1005
" 18	0.1002
" 19	0.0994
" 20	0.0991
Mean	0.0998

Nos. 21 and 22 show that even with the order of addition reversed, and with the extremely slow addition of magnesia mixture, the results are too high for large excess of precipitant, when the ammonium chloride is sufficiently reduced.

When magnesium chloride is added not in excess to solutions containing only a small quantity of free ammonia, or is thus added to those containing a large amount of free ammonia, some distinct quantity of phosphoric acid remains unprecipitated, as is well known. The same thing is true if an excess of magnesium chloride is added to a solution containing a large amount of free ammonia. Compare Nos. 8 and 9 with Nos. 15 to 20 inclusive. Filtrates from precipitations like Nos. 8 and 9 have, when examined for phosphoric acid, shown no trace, whereas in the class of precipitations represented by Nos. 15 to 20 inclusive a distinct reaction for phosphoric acid is obtained. This is not to be regarded as the solution of magnesium ammonium phosphate as such, but as the result of partial decomposition of this precipitate, at the moment of its formation by ammonia, with formation of ammonium phosphate and magnesia. The magnesia is dissolved by ammonium chloride if this is present in sufficient quantity, otherwise it remains to introduce plus error.

In large quantity of free ammonia then, the tendency to this reaction is more marked than in solutions containing only a small

quantity of free ammonia. Hence the reaction occurs only in nearly neutral solution when not reinforced by excess of magnesium chloride, whereas in solutions strongly ammoniacal, it occurs even if magnesium chloride is present in large excess. When magnesium chloride is added in excess too rapidly, or when the amount of ammonium chloride is much reduced, for either order of addition of ammonia and magnesium chloride some magnesia is precipitated. This occurs for too rapid addition, because as we may consider under this condition, a phosphate of magnesium is formed containing more magnesia than magnesium ammonium phosphate. It is conceivable that this may remain unchanged, giving too great weight after ignition, but I prefer to regard the reaction here, as being like that in the cases already considered. Thus the abnormal precipitate at the moment of its formation is partially decomposed by ammonia, and magnesium ammonium phosphate and magnesia are formed. If there is enough ammonium chloride present, and if the magnesium chloride is not added too fast, giving too rapid formation, the magnesia precipitated is redissolved as in cases already described. I do not regard the contamination by excess of magnesia mixture as mechanical.[1] The relative bulks of precipitates in Nos. 8 to 14 inclusive, a series carried out simultaneously, are against this idea, No. 14 being at least ten times the bulk of Nos. 8 or 9. Nos. 11 to 14 inclusive were the larger, and No. 14 the largest of the series. It is true that a bulky precipitate carries down more salt from solution than a crystalline one. In this regard the contamination is in part perhaps mechanical, but the bulk itself is not the chief cause, but an effect of contamination. Not only the size of such precipitates but their character show this.

[1] Gooch : *Am. Chem. J.*, 1, 391.

THE COLORIMETRIC ESTIMATION OF SMALL AMOUNTS OF CHROMIUM, WITH SPECIAL REFERENCE TO THE ANALYSIS OF ROCKS AND ORES.[1]

By W. F. Hillebrand.

Received April 14, 1898.

INTRODUCTION.

HAVING occasion to analyze a number of highly titaniferous magnetites containing chromium, phosphorus, and vanadium, it became a serious problem to effect satisfactory separations of all these bodies in a form fit for separate determinations. The method of T. Fischer[2]—digestion of the precipitated lead salts with a strong solution of potassium carbonate—appears to offer the long-needed satisfactory quantitative separation of arsenic, phosphorus, chromium, tungsten, and molybdenum from vanadium, the normal lead meta-vanadate remaining quite unattacked, according to the author, while the other lead salts are wholly decomposed, but the applicability of this method to the separation of the minute amounts often found in rocks and ores has not been tested. The time required is considerable, hence it was desirable to devise a more rapid way for determining both chromium and vanadium without resorting to this separation. That this object has been measurably achieved, with certain limitations as to vanadium, the work thus far done seems to indicate. The present paper will deal only with the rapid estimation of chromium either in absence or presence of any or all of the elements above mentioned.

In view of the high coloring power of the chromates, it is surprising that this property does not seem to have been made the basis for a quantitative method for the estimation of chromium. A search through some of the more important textbooks has revealed no reference to such a method, and I am unaware that one has even been suggested. Yet the results attainable by colorimetric comparisons of dilute alkaline solutions of unknown strength with those of a known standard, leave little to be desired in point of quantitative accuracy.

As with colorimetric methods in general this one gives better results with small than with large percentages of chromium, yet it can be applied in the latter cases with very fairly satisfactory

[1] Read before the Washington Section, March 10, 1898.

[2] Inaugural Dissertation, Rostock, 1894.

results by making a larger number of consecutive comparisons with the same solution.

OUTLINE OF METHOD.

The chromium is brought into a measured volume of solution as monochromate rendered alkaline by sodium carbonate, and the whole or a portion of this solution is then compared with a definite amount of a somewhat stronger standard likewise made alkaline with sodium carbonate. The latter is diluted with water till both seem to be exactly alike in color, when a simple calculation gives the amount of chromium sought. The actual comparison takes little time and any number of repetitions can be made if desired in order to secure greater accuracy from the mean of a large number of observations. The preparation of the solution to be tested offers nothing novel, but certain precautions have to be observed therein as well as in the color comparisons which will be touched upon later.

TESTING OF METHOD BY COMPARISON OF STANDARD SOLUTIONS.

Two standard solutions were prepared by dissolving 0.25525 and 0.5105 gram potassium chromate in one liter of water made alkaline by a little sodium carbonate, each cubic centimeter then corresponding respectively to one-tenth and two-tenths milligram chromic oxide, in which latter form chromium is usually reported in rocks and ores. Definite amounts of one of the standards were then diluted with varying amounts of water in a tall, square glass vessel with exactly parallel sides. Into an exact duplicate of this vessel five or more cc. of the standard were introduced from a burette and diluted with water from another burette till exact agreement seemed to be reached on looking through the glasses horizontally.

In the following tables are recorded all observations without regard to the sequence in which they were made. No greater pains were taken to get exact agreement of color than are ordinarily observed in our routine titanium estimations, which are carried out in a precisely similar manner, so that the results may be taken to represent every-day work without extreme precautions. In only two cases can the observations be considered really bad, *viz.*, the third comparison of No. 6 and the first of No. 16.

TABLE I.

Ten cc. standard represent one milligram chromic oxide.

	Test solution.		Comparison standard.						
No.	Standard. cc.	Diluted with water. cc.	cc.	H_2O added. cc.	Contents as chromic oxide. Milligrams.	Chromic oxide found. Milligrams.	Chromic oxide present. Milligrams.	Error. Milligram:	Chromic oxide. Per cent. found.
1	10[1]	90[1]	5	44.00	0.5	0.98	1	—0.02	98.0
2	20[2]	80[2]	5	21.00	0.5	1.92	2	—0.08	96.0
3	40	60	10	14.60	1.0	4.06	4	+0.06	101.5
4	40	60	9.7	14.25	0.97	4.05	4	+0.05	101.2
			10	13.95	1.0	4.17	4	+0.17	104.4
			10	14.30	1.0	4.11	4	+0.11	102.9
			10	14.20	1.0	4.13	4	+0.13	103.3
5	40	60	10	14.65	1.0	4.05	4	+0.05	101.4
			10	15.65	1.0	3.90	4	—0.10	97.5
6	40	60	10	15.25	1.0	3.96	4	—0.04	99.0
			10	14.30	1.0	4.11	4	+0.11	102.9
			10	13.15	1.0	4.32	4	+0.32	108.0
			10	14.75	1.0	4.04	4	+0.04	101.0
			20	29.50	2.0	4.04	4	+0.04	101.0
7	50	50	10	9.75	1.0	5.06	5	+0.06	101.2
8	50	50	10	10.00	1.0	5.00	5	0.00	100.0
9	60	40	10	7.20	1.0	5.81	6	—0.19	96.7
10	75	25	20	6.65	2.0	7.505	7.5	+0.005	100.1
			20	6.60	2.0	7.519	7.5	+0.019	100.2
			10	3.15	1.0	7.605	7.5	+0.105	101.4
			15	4.70	1.5	7.610	7.5	+0.11	101.5
11	10	10	10	10.15	1.0	0.992	1	—0.008	99.2
			20	19.75	2.0	1.006	1	+0.006	100.6
12	10	11	10	10.60	1.0	1.02	1	+0.02	102.0
13	14.2	26.9	10	18.60	1.0	1.43	1.42	+0.01	100.7
			20	35.70	2.0	1.47	1.42	+0.05	103.5
14	15	24.35	10	16.55	1.0	1.48	1.5	—0.02	98.7
15	16	20	10	13.30	1.0	1.54	1.6	—0.06	96.2
			20	24.30	2.0	1.63	1.6	+0.03	101.9
16	31.9	20.6	10.5	8.10	1.05	2.96	3.19	—0.23	92.8
			20.5	14.20	2.05	3.10	3.19	—0.09	97.2
17	62.05	22.3	20	7.00	2.0	6.25	6.205	+0.45	100.7
			40	12.00	4.0	6.49	6.205	+0.285	104.6

Mean percentage found, 100.5.

[1] Color in this dilution too faint.

[2] Limit of dilution for clear distinction of color in a thickness of three and three-tenths cm.

TABLE II.

Varying amounts of standard No. 2 (1 cc. = 0.2 mg. Cr_2O_3) diluted till of the same concentration as standard No. 1.

	Standard.						
No.	cc.	Water added. cc.	Contents as chromic oxide. Milligrams.	Chromic oxide found per 100 cc. Milligrams.	Chromic oxide present in 100 cc. Milligrams.	Error. Milligram.	Chromic oxide. Per cent. found.
18	5	5.2	1	9.80	10	—0.2	98.0
19	10	9.95	2	10.02	10	+0.02	100.2
20	15	15.8	3	9.74	10	—0.26	97.4
21	20	20.0	4	10.00	10	0.00	100.0
22	30	29.5	5	10.08	10	+0.08	100.8

Mean 99.3 Grand mean 100.36.

The first table and the grand mean show an apparent personal tendency toward slightly high results, though it is possible that this is due to a slight difference in the internal dimensions of the two glasses, the same one always having been used for the standard solution. If this is so, a long series of tests with glasses reversed should give a general mean slightly below 100.

TESTING THE METHOD ON ORES AND ROCKS.

In order to prove the value of the method in rock analysis, varying amounts of the standard solution were evaporated in a large crucible with five grams of an iron ore carrying phosphorus and vanadium, and fused with twenty grams of sodium carbonate and three grams sodium nitrate. The aqueous extract, after reduction of manganese by methyl or ethyl alcohol, was nearly neutralized by nitric acid and evaporated to secure approximate separation of silica and alumina. As a precautionary measure, since a little chromium is usually carried down, the precipitate was ignited, silica was removed by hydrofluoric and sulphuric acids, the residue was fused with sodium carbonate, and alumina again separated as before. To the combined filtrate was added mercurous nitrate and the slightly washed copious precipitate of phosphate, chromate, vanadate and carbonate of mercury was ignited with the paper in a platinum crucible, which can be done without much fear of loss or of injury to the crucible. The residue was then fused with a little sodium carbonate, extracted with

water, filtered into a graduated flask and made up to 50 or 100 cc., according to the intensity of the color, and compared with the standard. A similar operation was carried out with a silicate rock. Table III shows the results.

TABLE III.

No.	Chromic oxide added. Milligrams.	Chromic oxide found. Milligrams.
I. Five grams iron ore	7.03	7.18
	...	7.20
	...	7.25
	...	7.21
II. Five grams iron ore	2.99	3.08
	...	3.13
III. Two grams silicate	1.6	1.53
	...	1.57
	...	1.59

When the percentage of chromic oxide in an ore or mineral is more than about two-tenths per cent. and vanadium has not also to be estimated, much time may be spared by at once taking the color of the original extract from the sodium carbonate fusion, after insuring complete reduction and removal of manganese, and perhaps concentrating. But if the chromium is much less than this amount, and especially if several grams of powder have been operated on, it becomes difficult or impossible to obtain a filtrate of sufficiently small bulk to show a decided color. Therefore, in such cases, and when vanadium is likewise to be estimated, it is necessary to precipitate as above with mercurous nitrate in order to eventually have a small bulk of sufficiently colored solution. Even then, for very minute amounts, it is necessary to use Nessler tubes exactly as in ammonia estimations.

If niter has been used in the fusion and the crucible has been attacked by it, a yellow color of the filtrate may be due to dissolved platinum, but neither the proportion of niter nor the temperature of the blast should ever be high enough to permit the crucible to be attacked.

THE COLORIMETRIC APPARATUS AND ITS USE.

The glasses employed were of approximately square section, about twelve cm. high and three and three-tenths cm. inside meas-

urement, with exactly parallel sides, and of course as nearly alike as they could be obtained. One pair of opposite sides of each should be blackened. With glasses of the thickness mentioned it is generally advisable to use from five to ten cc. of standard at a time and to so regulate the strength of the solution to be tested that it shall contain more than two milligrams chromic oxide in 100 cc. which is about the limit of distinct visibility in a thickness of three and three-tenths cm.

In order to exclude the effect of side light in this and other similar methods (titanium for instance), it is very convenient to have a simple light box that can be easily held in one hand, about thirty-five cm. long and thirteen to fourteen cm. square, painted black inside and out and with one end closed by a piece of ground glass, the other open. For a space equal to the width of the glasses the cover is removed at the top next the glass end, to permit of the insertion of the glasses, side by side, in such a way that no light shall penetrate around their sides or between them. A stiffly sliding, black, cardboard shutter is movable up and down immediately back of the glasses, so that all light can be cut off except that which comes through the liquid.

Precautions of this kind are necessary if accurate results are to be counted on. Except for mere traces this simple combination of glasses and darkened box ensures greater accuracy and rapidity of work than Nessler tubes and is preferable likewise, so far as my own experience goes, to expensive instruments like the colorimeter of Soleil–Duboscq, etc. The glasses should, of course, have exactly parallel sides and equal diameters, though they may perhaps be made with advantage rather narrow in one direction to permit of using smaller bulks of liquid.

In making the color comparisons the box is best held close to a window, so as to get a full strong light. The condition of the light seems to make an appreciable difference in the accuracy of the comparisons, all of which were made by daylight.

ACCURACY OF RESULTS.

Especially for comparatively and very small amounts of chromium the method gives exact results, better than can ordinarily be hoped for from any gravimetric method, considering

the fact that as a rule other substances are present which it is extremely difficult to remove completely.

A few comparisons between colorimetric and gravimetric determinations of chromium in a few rocks are here given to show the order of agreement, the former having been made several months and even years after the latter.

Gravimetric. Per cent.	Colorimetric. Per cent.
trace	0.018
0.05	0.051
0.14	0.12
0.08	0.083
trace	0.013
none	0.0086
none	0.0067

The outcome was somewhat of a surprise, for it was scarcely to be expected that the long and laborious gravimetric separations should have resulted so well as they are shown to have done. It should be mentioned that for the gravimetric tests but one or two grams at most were used, which accounts for the reported absence of chromium in two instances, this report being based on the lack of color in the aqueous extract of the alkaline fusion after removal of manganese.

No experiments have been made with high percentages, but the tables give with certainty the degree of accuracy even then attainable. Whether the chromic oxide to be estimated is one-tenth per cent. or one hundred per cent., the percentage result is the same provided the dilution is alike in each case. For instance, if 99.5 per cent. is found in a total solution of 100 cc. containing 0.01 gram chromic oxide, the same percentage holds if the total volume were ten liters holding one gram chromic oxide.

It is probably inadvisable to increase the strength of the standard much above that of No. 2 above, containing two-tenths milligram chromic oxide in form of potassium chromate to the cubic centimeter.

No tests have been made with other alkaline solutions than sodium carbonate, in order to ascertain if there is a difference in the color intensities for like dilution, nor is it probably important to do so.

LABORATORY U. S. GEOLOGICAL SURVEY,
MARCH, 1898.

VOLUMETRIC ESTIMATION OF VANADIUM IN PRESENCE OF SMALL AMOUNTS OF CHROMIUM, WITH SPECIAL REFERENCE TO THE ANALYSIS OF ROCKS AND ORES.[1]

By W. F. Hillebrand.

Received April 14, 1898.

OUTLINE AND LIMITATIONS OF THE METHOD.

WHEN chromium and vanadium occur together and the former has been estimated colorimetrically as detailed in the preceding paper,[2] the vanadium can in many instances be at once estimated without separating from the chromium by the well-known method of titration with potassium permanganate in sulphuric acid solution after reduction by sulphurous acid and expulsion of all excess of the latter.

The application of the method is subject to one limitation—the chromium must not be present above a certain moderate amount. This limitation is due to the considerable amount of permanganate required to produce a clear transition tint when titrating in a hot solution, as is necessary with vanadium. In a cold solution of chromic sulphate much less permanganate is needed to produce the peculiar blackish tint without a shade of green, which affords a sure indication of excess of permanganate, but in a hot and especially a boiling solution the oxidation of the chromium[3] itself takes place so rapidly that a very large excess of the reagent may be added before a pronounced end-reaction is obtained. Nevertheless, as will be shown, quite satisfactory determinations of as little as one or two milligrams of vanadium pentoxide can be made in presence of as much as thirty milligrams of chromic oxide.

Inasmuch as chromium is almost never a prominent constituent of the clays, coals, iron ores, and rocks in which vanadium has been thus far reported, the method promises to be of great advantage in rock and ore analysis, where these elements probably frequently occur together, generally with phosphorus and sometimes arsenic. It is not directly applicable in

[1] Read before the Washington Section, April 14, 1898.

[2] This Journal, 20, 454.

[3] Storer, through Gmelin-Kraut, 2, [2] 290.

presence of molybdenum, and arsenic must first be removed by hydrogen sulphide if present.

TESTING THE METHOD.

A solution of sodium vanadate was prepared by fusing 0.937 gram of pure vanadium pentoxide with sodium carbonate and diluting to one liter. Each cubic centimeter contained 0.000937 gram vanadium pentoxide. Of this, sufficient amounts were mixed with varying volumes of a standard solution of potassium chromate. After in some cases determining chromium colorimetrically, sulphuric acid was added, sulphur dioxide gas[1] introduced for a few moments, and the excess of the latter expelled by boiling in a rapid current of carbon dioxide, without which its complete expulsion is difficult. When cooled to from 70°–80° C. the titration was made with very dilute solution of permanganate corresponding to about one milligram vanadium pentoxide to the cubic centimeter as calculated from its equivalent in iron. By repeating the reduction and boiling, any number of check-tests can be rapidly made in the same solution. The solutions ranged in bulk from 50 to 200 cc. according to the amounts of chromium added.

With the larger chromium contents the differences in the quantity of permanganate used, according as titration was effected at practically boiling temperature or a somewhat reduced one, were very apparent. In one case at nearly boiling heat, ten milligrams of chromic oxide were largely oxidized to chromium trioxide, as shown by the change of color from dark green to yellow. Even at 70°–80° with this amount of chromium the results for vanadium will be too high unless the precaution is taken to ascertain the needed correction by adding permanganate to an equal bulk of hot chromic sulphate solution containing approximately the same amount of chromium. When this is done, however, the results are satisfactory even when as much as thirty milligrams of chromic oxide are present and only one or two milligrams of vanadium pentoxide.

[1] The direct use of a solution of sulphur dioxide or of an alkaline sulphite is inadmissible unless these have been freshly prepared, since after a lapse of time they contain other oxidizable bodies than sulphurous acid or a sulphite. The sulphur dioxide is best obtained as wanted by heating a flask containing a solution of sulphur dioxide, or of a sulphite to which sulphuric acid has been added.

Doubtless the modified iodometric method of T. Fischer[1] will in general give sharper results where chromium is present in considerable amount, and if so it should be preferred to titration by permanganate. But its use involves the preparation of a standard thiosulphate instead of the ever-ready permanganate solution, and the manipulations are more time-consuming. The object has been in the present case to reach satisfactory results with the greatest expedition, and when chromium is not present in considerable amount this is accomplished.

The following tables contain the results of a considerable number of tests, those in Table II being tabulated separately in order to show the degree of accuracy attainable with a large excess of chromium by applying the correction above mentioned and also the amount of this correction.

TABLE I.

No.	Chromic oxide. Milligrams.	Vanadium pentoxide. Milligrams.	Vanadium pentoxide found. Milligrams.	Error. Milligram.
1	1	9.37	9.22	—0.15
2	1	0.94	1.04	+0.10
			0.98	+0.04
3	1.5	5.25	5.49	+0.24
			5.43	+0.19
4	2	5.62	5.5	—0.12
			5.5	—0.12
5	3	4.68	4.78	+0.10
			4.78	+0.10
			4.83	+0.15
6	3	5.62	5.58	—0.04
			5.58	—0.04
7	3.5	18.74	18.89	+0.15
			18.97	+0.23
8	6	5.6	6.1	+0.50
9	6	4.68	4.78	+0.10
10	6	5.62	5.58	—0.04
11	10	5.62	5.58	—0.04
12	10	23.52	23.81	+0.29
			23.71	+0.19
13	10	46.85	46.98	+0.13
			47.20	+0.35
14	25	23.52	23.65	+0.13
			23.75	+0.23
15	87.5	23.52	23.71	+0.19

[1] Inaugural Dissertation, Rostock, 1894, p. 33.

TABLE II.

Showing application of degree of correction for larger amounts of chromium, obtained by adding potassium permanganate to an equal bulk of solution containing a like amount of chromic sulphate.

No.	Chromic oxide. Milligrams.	Vanadium pentoxide. Milligrams.	Vanadium pentoxide found. Uncorr.	Vanadium pentoxide found. Corrected.	Error. Milligram.	Volume of solution.
16	20	0.94	1.59	0.99	+0.05	50–100 cc.
17	20	1.87	2.69	2.09	+0.22	"
			2.39	1.79	—0.08	
			2.59	1.99	+0.12	
18	20	18.74	19.4	18.73	—0.01	"
			19.3	18.63	—0.11	
			19.3	18.63	—0.11	
19	30	1.87	2.99	2.14	+0.27	About 100 cc.
			2.79	1.94	+0.07	
			2.79	1.94	+0.07	
			2.69	1.84	—0.03	
			2.69	1.84	—0.03	
20	30	1.87	2.69	1.79	—0.08	200 cc.
			2.89	2.09	+0.22	
			2.89	2.09	+0.22	
			2.79	1.89	+0.12	
21	62	46.85	48.60	47.60	+0.75	200 cc.

In spite of the fact that the correction in most of the trials of this last table represents a large proportion of the permanganate used, the results must be considered satisfactory in view of the small amount of vanadium present, and they show that the method in competent hands after a little experience affords trustworthy figures.

TESTING THE METHOD ON ROCKS AND ORES.

The following table shows its availability for rocks and ores. Known amounts of both chromium and vanadium were added to an iron ore and to a silicate, both free from arsenic, which were then fused with sodium carbonate and nitrate and further treated as follows: After extracting with water and reducing manganese by alcohol, the silica and alumina were mostly removed by nearly neutralizing with nitric acid and evaporating to near dryness. The washed precipitate was ignited and treated with hydrofluoric and sulphuric acids, the residue fused with sodium carbonate, since it frequently contains a little chromium, and

again nearly neutralized, etc. To the combined and slightly alkaline filtrates was added mercurous nitrate, the precipitate of phosphate, vanadate, chromate, and carbonate was ignited in platinum, fused with a little sodium carbonate, leached with water, and filtered into a small graduated flask. After colorimetric determination of the chromium, sulphuric acid was added, both chromium and vanadium were reduced by sulphur dioxide gas, and the titration carried out as described.

TABLE III.

No.	Chromic oxide. Milligrams.	Vanadium pentoxide. Milligrams.	Vanadium pentoxide found. Milligrams.	Vanadium pentoxide. Error. Milligram.
22	7	6.76	6.81	+0.05
(Five grams iron ore)			6.48	—0.28
			6.43	—0.33
			6.37	—0.37
23	3	3	3.08	+0.08
(Five grams iron ore)			3.13	+0.13
			3.03	+0.03
			3.08	+0.08
24	1.6	1.87	1.86	—0.01
(Two grams silicate)			1.97	+0.10
			2.07	+0.20
			1.86	—0.01

These and other experiments show that by taking not over five grams of ore or rock, vanadium, if present to the extent of 0.01 or 0.02 per cent., can be readily estimated by exercising reasonable care in all the operations. Absolute confirmation of its presence can be easily obtained by evaporating and igniting the solution to remove excess of sulphuric acid, taking up with a few drops of dilute nitric acid, and adding to the solution in a test-tube a drop or two of hydrogen peroxide. In this way positive or negative assurance as to the presence of vanadium, is given when the result of titration alone might be uncertain. Addition of ether at the same time affords a simultaneous test for chromium by its blue color, and this might perhaps be made use of, if necessary, to remove all, or the greater part of the chromium from the titration of the vanadium, since the oxidation product of the latter does not dissolve in the ether.

It is even possible that the dark brown color produced by hydrogen peroxide might be utilized for an exact colorimetric method for estimating vanadium.

LABORATORY OF THE U. S. GEOLOGICAL SURVEY.
APRIL, 1898.

NOTES.

The Liquefaction of Hydrogen and Helium.—A recent issue of the London *Times* states that Professor Dewar has liquefied both these gases at the Royal Institution. Hydrogen was produced to the amount of half a wineglassful in five minutes. The specific gravity of the liquid is stated as 0.6. The boiling-point of helium appears to be not very far from that of hydrogen.

The International Congress of Applied Chemistry.—The Organizations Committee of the Third International Congress of Applied Chemistry, to be held at Vienna, beginning July 28, begs to inform American chemists who propose to take part in that Congress, that a committee has been formed for the purpose of securing agreeable and cheap dwelling places for foreign members during the continuance of the Congress. Those wishing to engage such places should address: Wohnungscomite des III internationalen Congresses für angewandte Chemie, Wien IV/2 Schönburgstrasse 6.

The Organizations Committee also begs to inform American chemists that, on account of the Jubilee Exposition to be held in Vienna from the 7th of May to the 8th of October, this year, the Austrian railroads are prepared to furnish round-trip tickets to all points in Austro-Hungary at greatly reduced prices. A further communication from the Railroad Committee of the Third International Congress will be made to American chemists in a short time concerning this important matter.

I am also requested by Prof. Strohmer, the General Secretary of the Third International Congress of Applied Chemistry, to inform American chemists that the North German Lloyd Steamship Company has made the following reductions in fares to members to the Congress desiring to use its steamships during the coming summer.

Rates of fares are fixed for two seasons; *viz:* From the first of April to the first of November, called the summer season, and from the first of November to the 31st of March, called the winter season. The reduced rates for the two seasons are as follows:

	Summer season.	Winter season.
For Steamships Kaiser Wilhelm der Grosse and Kaiser Friedrich	$105.00	$77.50
All other express steamers except those mentioned above	100.00	77.50
For Steamships Barbarossa, Friedrich der Grosse, Königin Luise and Bremen	80.00	65.00
All other mail steamers except those mentioned	75.00	60.00

Arrangements should be made with the local representatives of the company, or with the New York agents, to secure the proper reduction. The presentation of the membership card will be sufficient evidence of the right of the applicant to secure the reduced rates.

No information has been sent in regard to further reductions for round-trip tickets. Arrangements, if any, for these reductions should be made with the agents of the company. The prices given above are for the best rooms of the first class, and the Steamship Company will accord to members of the Congress the best quarters if application be made in time.

H. W. WILEY,
Chairman American Committee.

ERRATUM.

The Volatility of Titanic Oxide. — Mr. W. F. Hillebrand, Washington, D. C., has called attention to an erroneous statement in the paper on "The Commercial Analysis of Bauxite."[1] It is that titanic oxide is volatile under the action of a mixture of sulphuric and hydrofluoric acids. This is a mistake. There is a very trifling loss of titanic oxide when a mixture of these two acids is employed, and it arose from a misinterpretation of some notes, for which Mr. Hancock is in no wise responsible. I am obliged to Mr. Hillebrand for drawing attention to this error.

WM. B. PHILLIPS.

BOOKS RECEIVED.

1. Variation in the Amount of Free and Albuminoid Ammonia in Waters on Keeping. 2. Corrosion of Aluminum. 3. Crystallized Carbon Dioxide. 4. On the Internal Structure of Gold Nuggets. 5. Contribu-

[1] This Journal, 20, 209.

tions to the Bibliography of Gold. By A. Liversidge, Professor of Chemistry, University of Sidney, N. S. Wales. 22 pp.

Methods for the Analysis of Ores, Pig Iron, and Steel in use at the Laboratories of Iron and Steel Works in the Region about Pittsburg, Pa., together with an Appendix Containing Various Special Methods for Analysis of Ores and Furnace Products. Contributed by the Chemists in Charge, and Edited by a Committee of the Chemical Section, Engineers' Society of Western Pennsylvania. Easton, Pa.: The Chemical Publishing Co. 1898. v + 133 pp. Price: cloth, $1.00; paper, 75 cents.

Animal Fats and Oils. By Louis Edgar Andés. Translated by Charles Salter. 62 illustrations. xii + 240 pp. 1898. New York: D. Van Nostrand Co. Price, $4.00.

The John Crerar Library. Third Annual Report for the Year 1897.

Preparation and Application of Fungicides. Bulletin 125, Connecticut Agricultural Experiment Station, New Haven, Conn.

The Truth about Cigarettes. Papers read and discussed by The Medico-Legal Society. 48 pp. Price, 10 cents.

Bulletin No. 43. I. Soils. II. Climate. III. Water Supply. IV. Irrigation Equipment. Report from Beeville Station. April, 1897. 30 pp. Texas Agricultural Experiment Station, College Station, Brazos Co., Texas.

Bulletin No. 44. Paints and Painting Materials and Miscellaneous Analyses. July, 1897. 15 pp. Texas Agricultural Experiment Station, College Station, Brazos Co., Texas.

Administrative Report of the State Geologist from October 24, 1894, to October 15, 1896, inclusive. 45 pp. and five half-tone plates. Administrative Report of the State Geologist for the Year Ending October 15, 1897. 20 pp. and three half-tone plates. W. S. Yeates, State Geologist. Geological Survey of Georgia, Atlanta, Georgia.

A Preliminary Report on the Marbles of Georgia. By S. W. McCallie, Assistant Geologist. Bulletin No. 1, 1894. 92 pp., with numerous half-tones and maps. 1894. Geological Survey of Georgia, Atlanta, Ga.

A Preliminary Report on the Corundum Deposits of Georgia. By Francis P. King, Assistant Geologist. 138 pp., with half-tones and maps. 1894. Geological Survey of Georgia, Atlanta, Ga.

A Preliminary Report on a Part of the Water-Powers of Georgia. Compiled from the notes of C. C. Anderson, Late Assistant Geologist, and from other sources. By B. M. Hall, Special Assistant. 1896. 153 pp., with half-tones and maps. Geological Survey of Georgia, Atlanta, Ga.

A Preliminary Report on a Part of the Phosphates and Marls of Georgia. By S. W. McCallie, Assistant Geologist. 103 pp., with half-tones. 1896. Geological Survey of Georgia, Atlanta, Ga.

Constitution of the New England Association of Chemistry Teachers, adopted February 19, 1898, Lyman C. Newell, President, and Irving O. Palmer, Newtonville, Mass., Secretary.